KINETICS OF ELECTRODE PROCESSES AND NULL POINTS OF METALS

L. I. ANTROPOV

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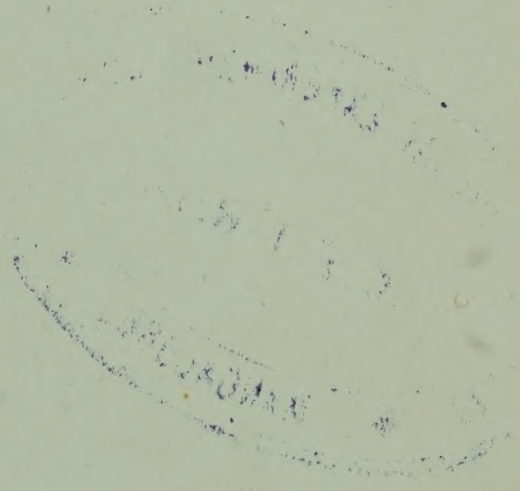

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KINETICS OF ELECTRODE PROCESSES AND NULL POINTS OF METALS

by

L. I. ANTROPOV

Unesco Expert

Indian Institute of Technology, Bombay

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

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FOREWORD

IN the month of January 1958, Professor L. I. Antropov delivered a series of lectures and stimulated considerable thought and discussion among the scientific workers of the Central Electrochemical Research Institute, Karaikudi. Professor Antropov's versatile knowledge and his sure understanding of practical electrochemical problems made us feel that the Council of Scientific & Industrial Research would be doing a service to electrochemistry by presenting these lectures in the form of a book.

The essence of Professor Antropov's point of view is that the electrical charge on an electrode surface and the structure of the electrical double layer play a crucial role in electrode processes.

Professor Antropov devotes the first two chapters to developing the φ-scale of electrode potentials (which is a measure of the charge on the electrode); and to a short but lucid treatment of the mechanism of hydrogen overpotential. The fundamental ideas so developed provide a fresh approach of considerable power and relevance particularly to three important fields of applied electrochemistry — metal deposition, electro-organic reductions and corrosion.

Clearly and cogently expounded, Professor Antropov's viewpoint deserves careful attention and close consideration by all electrochemists. It is, therefore, a great pleasure for me to introduce this publication particularly because the information presented in these lectures is not readily available in the English language.

Karaikudi
September 21, 1959

K. S. G. Doss
Director

PREFACE

THE main purpose of this publication is to give a brief survey of the theory of electrode processes in a form which may be helpful in dealing with electrochemical problems of practical interest. As a result, the treatment of many aspects is more qualitative than quantitative in character.

The basic viewpoint I have tried to put forward is that the null point of metals and the mechanism of hydrogen overvoltage play a very important part in the kinetics of electrochemical reactions. Accordingly, I have discussed, in the first two chapters, the φ-scale of electrode potentials, based as it is on the null point of metals, and the theory of the cathodic evolution of hydrogen.

It is possible that, in some cases, the views expressed here may contradict those expressed elsewhere. This is to some extent inevitable, as one of the reasons for writing this review is to give an account of the investigations that I have made in association with my collaborators.

During my stay in India as an Unesco expert attached to the Indian Institute of Technology, Bombay, I have had the opportunity to deliver a course of lectures at Kharagpur, Karaikudi, Bombay, Bangalore and Poona. On all these occasions I had the privilege of discussing various questions with the Indian scientists working in this field. I feel greatly indebted to them for the many useful suggestions made in the course of these discussions. This book is indeed an outcome of the lectures I have had the pleasure to deliver in India.

My cordial thanks are due to Dr. K. S. G. Doss, Director, Central Electrochemical Research Institute, Karaikudi, for having kindly agreed to go through the manuscript and for the editorial remarks as also for the many helpful discussions we had on some of the problems dealt with in this book.

I am also indebted to my friends, Mr. Karmanov and Mr. Kuzmin, for their assistance in the many language difficulties I have had in the course of writing this book.

I am grateful to the authorities of the Indian Institute of Technology, Bombay, for giving me the opportunity to deliver lectures at various centres of education and research in India and for their encouraging and helpful attitude which I could so well appreciate while preparing this book.

Bombay L. I. ANTROPOV
September 9, 1959

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CHAPTER ONE

THE "φ-SCALE" OF ELECTRODE POTENTIALS

Definition. It is well known that when a metal is immersed in a solution containing a salt of the metal, an interchange of ions takes place between the two phases. At the beginning of this process, the velocities of transfer of ions in the two opposite directions may not be the same and, therefore, when the equilibrium state is reached, the metallic surface attains an excess of charge in relation to the solution. This charge may be positive, negative or it may be equal to zero.

The difference of potential which is established between the metal and the solution — the so-called single electrode potential — can neither be measured directly nor calculated theoretically. Normally the e.m.f. of some electrochemical cell which consists of two electrodes has to be determined. In this cell one of the electrodes is arbitrarily chosen as a reference electrode and the value of its potential is assumed to be known. The values of electrode potentials obtained in this manner are relative and depend on the reference electrode.

If the standard hydrogen electrode is taken as the reference electrode, the potentials would be given on the hydrogen scale, which will be referred to as the ϵ-scale of potentials. There is no definite connection between the ϵ-potential of a metal and its charge (q). The sign and value of the ϵ-potential only show the relation in which the given electrode stands to the hydrogen electrode. If for two different metals (M_1 and M_2) the potentials ${}_{M_1}\epsilon$ and ${}_{M_2}\epsilon$ are equal, this indicates the existence of a thermodynamic equilibrium between them; but it does not mean the equality of charges q_1 and q_2.

No scale of potentials based on a particular reference electrode can give any indication of the sign and magnitude of the charge on the metal. But, for electrochemical kinetics, the

charge on the metal with respect to the solution is of primary importance. In this connection a new scale of electrode potentials has been developed[1-5]. As the basis of this scale, referred to hereinafter as the "φ-scale", the potential of zero charge (null point) of the metal ($\epsilon_{q=0}$) has been taken. The null point of the metal corresponds to the value of the potential at which the charge on the metal is equal to zero with respect to the solution in the absence of any surface active compounds. All values of potentials are given in relation to the null point of the metal, and hence, each metal will have its own scale of potential based on its own null point.

Every value of potential φ is a difference between the potential of the metal under the given conditions and the corresponding value of $\epsilon_{q=0}$. Thus, the standard potential of the metal in the new scale will be

$$\varphi^\circ = \epsilon^\circ - \epsilon_{q=0}$$

where ϵ° and $\epsilon_{q=0}$ are given in the same relative scale. For example,

$$_{Zn}\varphi^\circ = {}_{Zn}\epsilon^\circ - {}_{Zn}\epsilon_{q=0}$$

$$_{Fe}\varphi^\circ = {}_{Fe}\epsilon^\circ - {}_{Fe}\epsilon_{q=0}$$

$$_{Cd}\varphi^\circ = {}_{Cd}\epsilon^\circ - {}_{Cd}\epsilon_{q=0} \text{ etc.}$$

It is self-evident that the φ-potential thus defined does not depend on an arbitrarily chosen relative scale of potentials.

Null Points of Metals. For determining the values of φ-potentials it is necessary to know the values of $\epsilon_{q=0}$. The first information on the null points of metals was obtained with the help of electrocapillary curves. The maximal value of surface tension of a metal-solution interface, i.e. the maximum of the electrocapillary curve corresponds to the potential of zero charge on the metal (Fig. 1). This follows particularly from Lippmann's first equation

$$\frac{d\sigma}{d\epsilon} = -q_s \qquad (1)$$

where σ, ϵ and q_s are the interfacial tension, the potential of the metal-solution interface and the charge of the solution respectively.

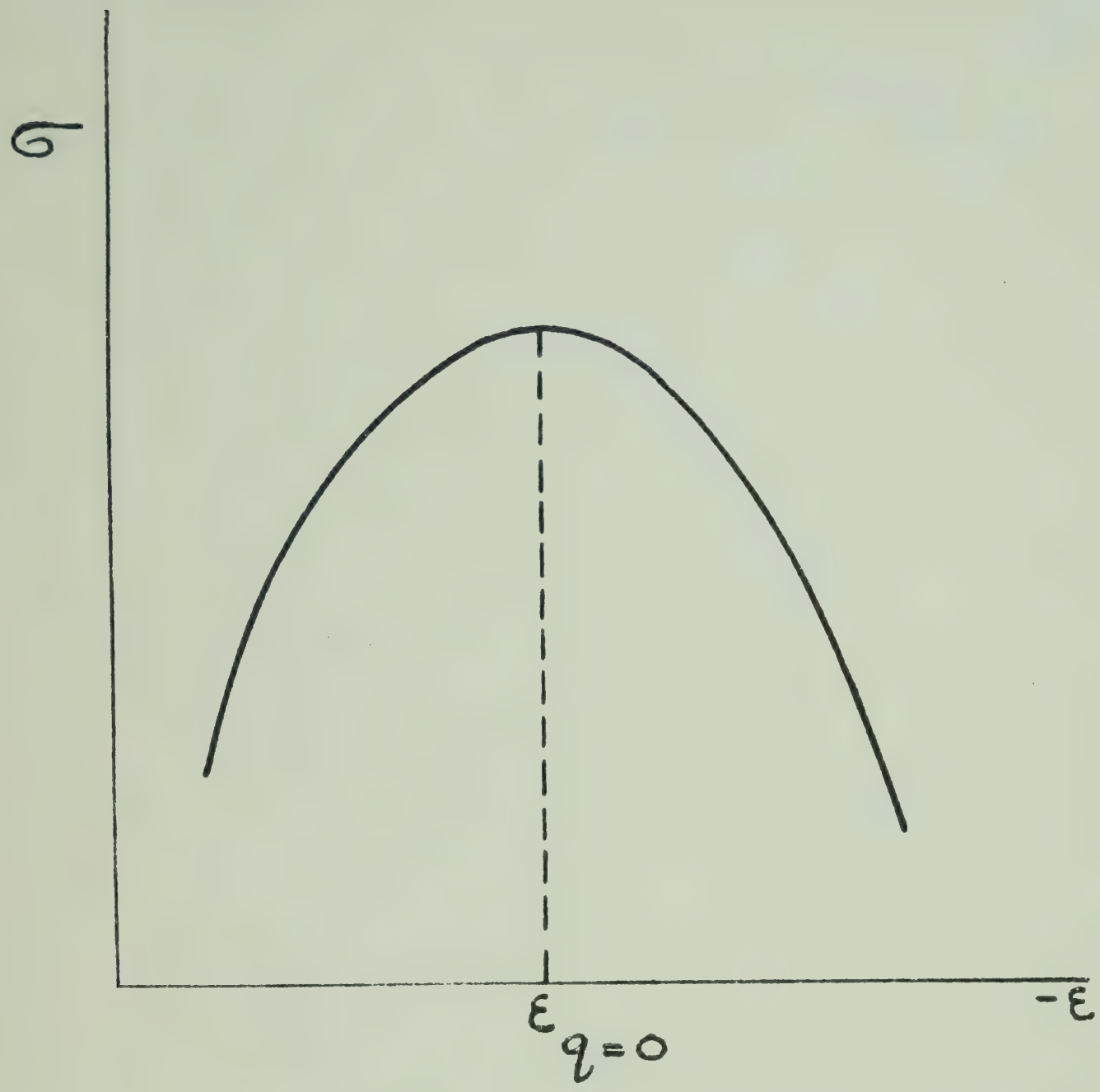

FIG. 1—ELECTROCAPILLARY CURVE OBTAINED IN A SOLUTION DEVOID OF ANY SURFACE ACTIVE COMPOUNDS

This method is applicable only to liquid metals or to metals in the molten state. However, from Lippmann's second equation

$$-\frac{d^2\sigma}{d\epsilon^2} = \frac{dq}{d\epsilon} = K_e \qquad (2)$$

it may be seen that the relation between the differential capacity of the double layer (K_e) and potential may be used for experimental estimation of the null point. The minimum in the curves of K_e against ϵ corresponds to the null point of the metal (Fig. 2).

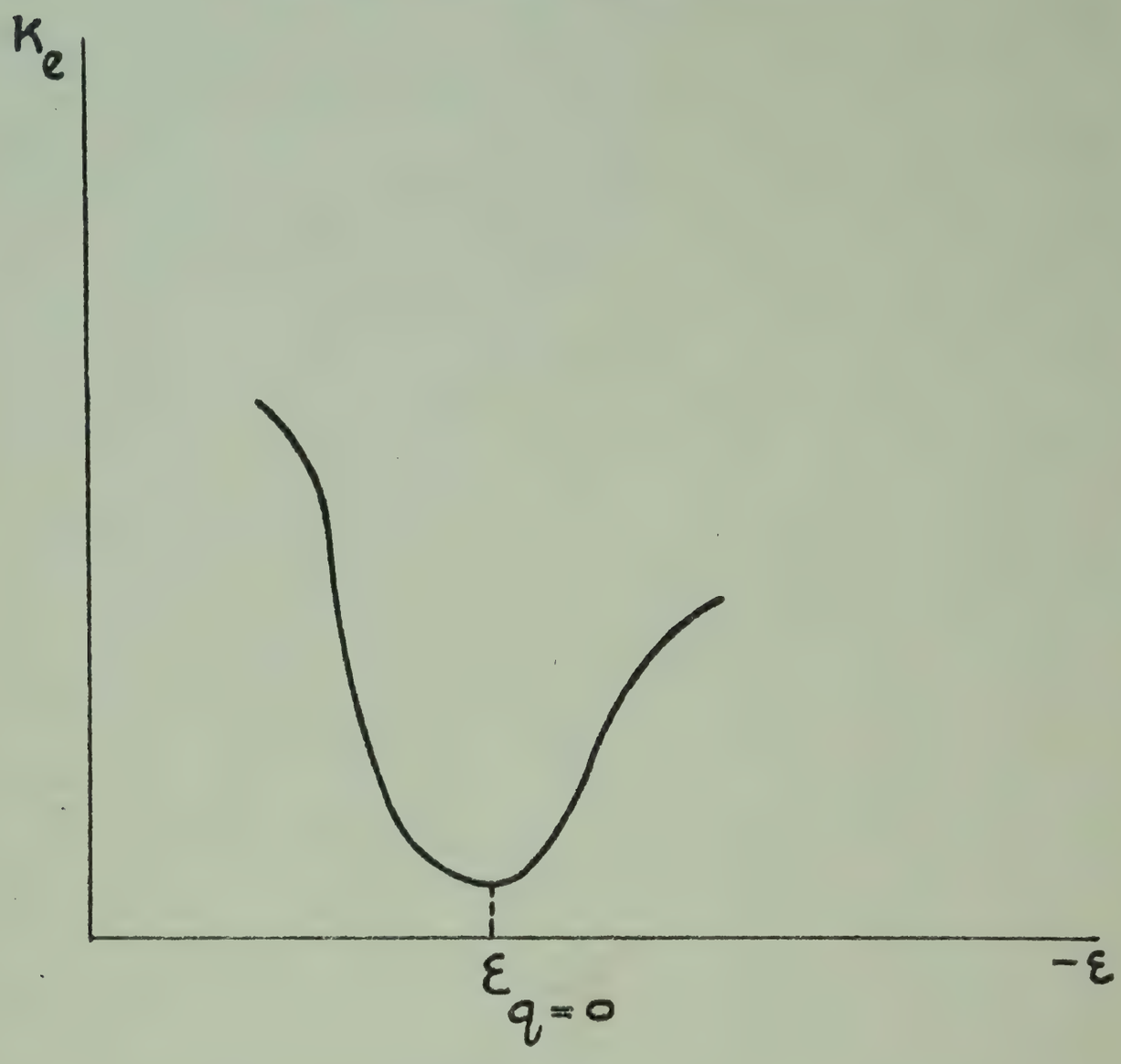

FIG. 2 — A SCHEMATIC REPRESENTATION OF THE RELATION BETWEEN DIFFERENTIAL CAPACITY OF THE ELECTRIC DOUBLE LAYER AND THE ELECTRODE POTENTIAL

The null points of various metals estimated by these and some other methods are recorded in Table 1.

The values of $\epsilon_{q=0}$ can be determined in some cases with a degree of accuracy not higher than 0·1 to 0·2 volt, but as will be seen later, this is quite sufficient for many applications of the φ-scale.

Physical Meaning of Electrode Potentials in the φ-scale. The physical meaning of electrode potentials in the φ-scale may be found in the following way[5]. The electrolytic cell, shown in Fig. 3, consists of two metals M and M'. The e.m.f. of this cell (E) is a sum of three outer potentials: ${}_{MM'}\varphi$ (the potential difference between two points in metals M and M'), ${}_{M'S}\varphi$ (the potential difference between the points in metal M' and

TABLE 1 — NULL POINTS OF METALS[5]

METAL	METHOD	$\varepsilon_{q=0}$	REMARKS
Na/Hg*	Dropping electrode	−1·79	
Tl	Differential capacity	−0·82	
Cd†	Electrocapillary curves for molten metal	−0·72	
Pb	Differential capacity, electrocapillary curves for molten metal	−0·67	Average value
Zn	Surface hardness, electrocapillary curves for molten metal†	−0·64	Average value
Ga	Electrocapillary curves	−0·60	
Co	Work function	−0·51	$W_e = 4{\cdot}20$ eV
Zn/Hg*	Dropping electrode	−0·46	
Cr	Contact angle	−0·45	
Al	Electrocapillary curves for molten metal†	−0·40	
Tl/Hg*	Dropping electrode	−0·36	
Sn†	Electrocapillary curves for molten metal	−0·34	
Cd/Hg*	Dropping electrode	−0·34	
Hg	Different methods	−0·21	
	Dropping electrode	−0·19	
Cu/Hg*	Dropping electrode	−0·18	
Fe	Work function	−0·02	$W_e = 4{\cdot}77$ eV
Ag	Differential capacity	0·05	
Cu	Contact angle	0·10	Average value
C_{act}	Adsorption	0·20	Average value
Ni	Work function	0·21	$W_e = 5{\cdot}03$ eV
Pt/H	Adsorption, contact angle	0·25	Average value
Te	Surface hardness	0·61	
Pt/O	Adsorption	1·50	Average value

*Molar fraction of metal in amalgam, 0·01[6,7].

†Found on the assumption that the null point of mercury does not depend on the state of salt (solution or molten state) and does not change with temperature[5].

solution S), and ${}_{SM}\varphi$ (the potential difference between the points in solution S and metal M)[8,9]

$$E = {}_{MM'}\varphi + {}_{M'S}\varphi + {}_{SM}\varphi \qquad (3)$$

Let it be assumed that the e.m.f. of this cell is equal to the φ-potential of M'. Then, M and M' ought to be two pieces of the same metal and ${}_{MM'}\varphi$ will be equal to zero. Each of the metal-solution Galvani potentials may be represented as a result of transition of ions through the metal-solution interface and orientation of dipoles on the same interface, thus:

$${}_{SM}\varphi = {}_{SM}\varphi_{ion} + {}_{SM}\varphi_{dip} \qquad (4)$$

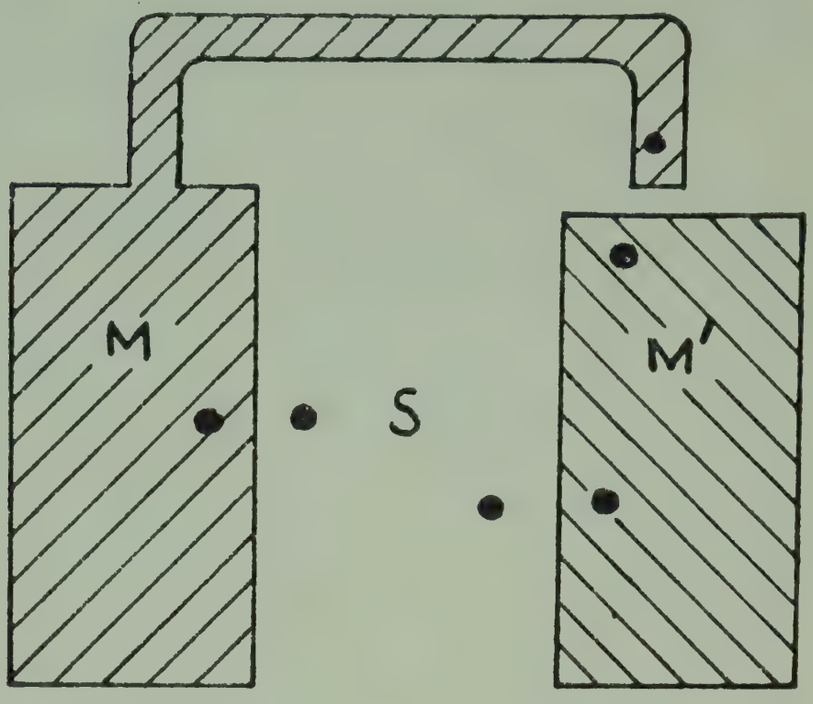

FIG. 3 — ELECTROLYTIC CELL CONSISTING OF TWO PIECES (M AND M'), OF A METAL DIPPED IN A SOLUTION (S). ONE OF THE TWO PIECES IS BROUGHT UP TO A POTENTIAL EQUAL TO THE NULL POINT OF THE METAL

But to satisfy the above assumption the potential of one of the metals (e.g. M) under these conditions should correspond to the null point of this metal. In this case, the ${}_{SM}\varphi_{ion}$ will be equal to zero and

$$ {}_{M'}\varphi = E = {}_{M'S}\varphi_{ion} + {}_{M'S}\varphi_{dip} - {}_{MS}\varphi_{dip} \qquad (5) $$

This means that the potential of the metal given in the φ-scale is a measure of the charge on the metal and of the alteration in degree of orientation of polar molecules on the metal-solution interface. At the null point, when the surface of the metal is uncharged, the minimum degree of orientation ${}_{MS}\varphi_{dip}$ may be expected. If the charge on the metal is no more equal to zero, but is positive, then the change of orientation of dipoles will increase the negative charge of the layer of solution in contact with the metal surface. In the case of a negatively charged metal, the change of orientation will be opposite in direction. Therefore, the sign of the φ-potential will be always the same as the sign of the charge of metal with respect to the solution.

φ-Potential and Structure of the Electrical Double Layer on Metal-solution Interface. There is a close relation between the value and sign of the φ-potential and the structure of a double layer. This relation is illustrated by Figs. 4 to 6 representing a somewhat simplified picture of an electrical double layer in three cases: (i) $\varphi>0$; (ii) $\varphi=0$, and (iii) $\varphi<0$. In case (i) the charge of the metal is positive, the anions are adsorbed on the metal surface and the negative parts of the dipoles are turned towards the metal. When $\varphi=0$, the charge of the metal is also equal to zero, and no pre-eminent physical adsorption takes place. If $\varphi<0$, the metal will be charged negatively, cations are attracted by the metal surface and oriented adsorption of the dipoles with their negative ends facing away from the metal takes place.

To illustrate the difference between the hydrogen-scale and the φ-scale of potentials, we will consider the standard potentials of Zn, Fe and Cd:

$$_{Zn}\varphi^{\circ} = -0{\cdot}76 - (-0{\cdot}64) = -0{\cdot}12 \text{ V}$$

$$_{Fe}\varphi^{\circ} = -0{\cdot}44 - (-0{\cdot}02) = -0{\cdot}42 \text{ V}$$

$$_{Cd}\varphi^{\circ} = -0{\cdot}40 - (-0{\cdot}72) = +0{\cdot}32 \text{ V}$$

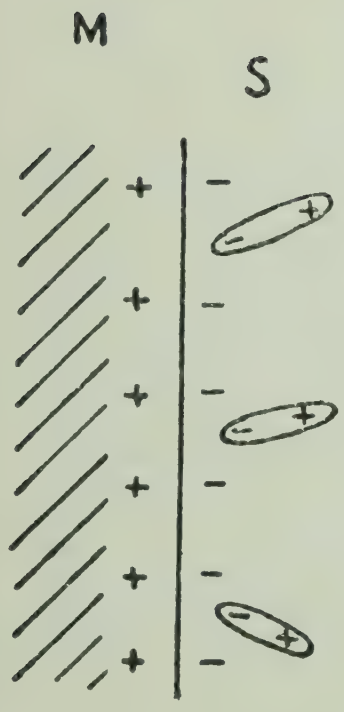

FIG. 4

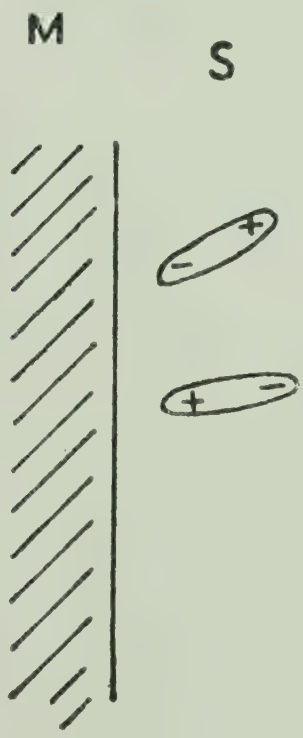

FIG. 5

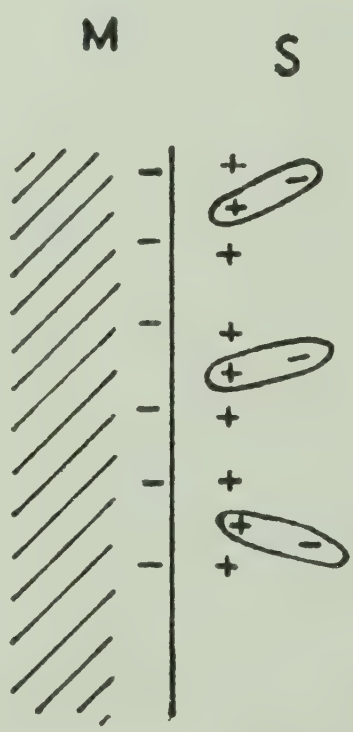

FIG. 6

FIGS. 4-6—4. A SIMPLIFIED PICTURE OF THE ELECTRICAL DOUBLE LAYER ON THE METAL-SOLUTION INTERFACE, WHEN $\varphi>0$. 5. A SIMPLIFIED PICTURE OF THE ELECTRICAL DOUBLE LAYER ON THE METAL-SOLUTION INTERFACE, WHEN $\varphi=0$. 6. A SIMPLIFIED PICTURE OF THE ELECTRICAL DOUBLE LAYER ON THE METAL-SOLUTION INTERFACE, WHEN $\varphi<0$

The standard potentials of all the above metals given in the hydrogen scale are negative. However, as can be seen from their φ-potentials, the charge of cadmium with respect to the solution is positive; the charge of zinc, the most negative metal in this series, is not very far from zero; and only in the case of iron is the charge on the metal surface negative.

For two metals (Fe and Cd) with approximately the same values of ϵ°-potentials, the charge on the surface and the structure of the double layer can be quite different. But if for two metals the values of φ-potentials are the same, it will indicate that their charges are approximately equal and the structures of the double layers in both these cases are very similar. This gives a possibility of comparing the experimental data obtained in the kinetic study of different metals.

CHAPTER TWO

HYDROGEN OVERPOTENTIAL

Definition and Origin. The overall reaction of hydrogen evolution may be represented by

$$2H_3O^+ \xrightarrow{2e} 2H_2O + H_2 \qquad (A)$$

This reaction is very important not only in connection with the electrolytic production of hydrogen on an industrial scale, but also because it takes place along with and influences many other electrochemical processes. We shall not present here a detailed picture of hydrogen evolution; and, therefore, only those aspects, which seem to be necessary for a better understanding of various electrochemical processes will be considered.*

Usually it is assumed that the overall reaction (A) consists of at least two stages:

$$H_3O^+ \xrightarrow{e(M)} H_{ads} \longrightarrow \tfrac{1}{2}\, H_2 \qquad (B)$$

The first stage is a discharge of ions on the surface of the metal, resulting in the formation of adsorbed hydrogen atoms. The second stage is a combination of the adsorbed hydrogen atoms to form hydrogen molecules. Either of these stages can be a slow one, and may be the rate-determining step in the overall reaction.

Due to the slowness of either of the two stages, the cathodic evolution of hydrogen occurs at potentials more negative than the reversible potential given by the Nernst formula. The difference of the reversible potential (ϵ) and the irreversible potential (ϵ_j) corresponding to a definite current density (j) is called the hydrogen overpotential and it is normally denoted by the symbol η. Thus

$$\epsilon - \epsilon_j = \eta \qquad (6)$$

---

*For more comprehensive treatment, cf. Frumkin *et al.*[10] and Prockris *et al.*[11].

The hydrogen overpotential η is a function of the current density, the nature of the metal, the temperature and composition of the solution, and the nature of solvent.

In 1905 Tafel found an empirical relationship between hydrogen overpotential and current density. This relationship is known as Tafel's formula:

$$\eta = a + b \log j \tag{7}$$

This formula may be derived by assuming that either of the two stages of reaction (B) is slow.

Slow Combination of Adsorbed Hydrogen Atoms. If the slow combination is the cause of overpotential, there will be no equilibrium between adsorbed hydrogen atoms and gaseous molecules of hydrogen. But at the same time there has to be an equilibrium between adsorbed and gaseous hydrogen atoms. Therefore, to determine the potential of an electrode on which the free atoms of hydrogen in the gaseous phase are in equilibrium both with adsorbed H-atoms and dissolved H^+-ions, the expression

$$\epsilon_{H^+/H} = \epsilon^\circ_{H^+/H} + \frac{RT}{F} \ln \frac{C_{H^+}}{C_H} \tag{8}$$

has to be used.

Each value of the pressure of hydrogen atoms will correspond to a definite value of the surface concentration of adsorbed hydrogen atoms and vice versa. If the combination is a slow stage, the surface concentration of hydrogen atoms (C'_H) at any given current density ought to be higher than that in the equilibrium state. In accordance with this, the concentration of hydrogen atoms in the gaseous phase ($_jC_H$) should be also increased and the potential at the electrode will be more negative than the reversible potential

$$\epsilon_{H^+/H} = \epsilon^\circ_{H^+/H} + \frac{RT}{F} \ln \frac{C_{H^+}}{{}_jC_H} \tag{9}$$

where ${}_jC_H > C_H$.

The rate of combination, when the steady state is attained, will be equal to the value of current density:

$$j = k'_j C'^2_H$$

or if the Freundlich isotherm is valid,

$$j = k' K_{fj} C^{2\beta}_H \tag{10}$$

where $0 < \beta < 1$.

By substituting the equation for ${}_jC_H$ into (9), the resulting overpotential is represented by

$$\eta = -\frac{RT}{2\beta F} lnk' K_f C_H + \frac{RT}{2\beta F} lnj \qquad (11)$$

or $\eta = a + b \log j$.

The Tafel constants a and b are expressed by

$$a = \frac{RT}{2\beta F \ 0{\cdot}43} \log k' K_f C_H,$$

$$b = \frac{RT}{2\beta F \ 0{\cdot}43}$$

In the above equations K_f and β and, therefore, a and b also are functions of the nature of the cathodic metal.

Expression (11) is simplified to some extent since it does not take into account the polar nature of the bond *M-H*. The energy of the bond *M-H* is a function of the electrode potential, which in its turn depends on the composition of the solution, and particularly on the *p*H. It is to be expected, therefore, that in the case of retarded combination the overpotential will also be a function of solution composition.*

Slow Discharge of Hydrogen Ions. If the discharge of hydrogen ions is a rate-determining process, the structure of the electrical double layer on the metal-solution interface will be very important. The best approximation to the real picture of a double layer has been given in Stern's theory.†

According to this theory the solution side of a double layer consists of two parts: condensed and diffuse (Fig. 7). The condensed region extends up to the distance r_o which is of the order of ionic dimensions. In this region, the ions are supposed to be specifically or electrically adsorbed, while in the diffuse part they are distributed under the influence of both electric forces and thermal motion forces.

It is assumed[13] that the discharge of ions takes place at a distance approximately r_o from the electrode surface. This means that only adsorbed H^+ ions can be discharged, and that

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*This cannot be, however, of great importance[12].

†For a recent modification of Stern's theory, the reader may refer to Grahame, D. C., *Chem. Rev.*, **41** (1947), 441.

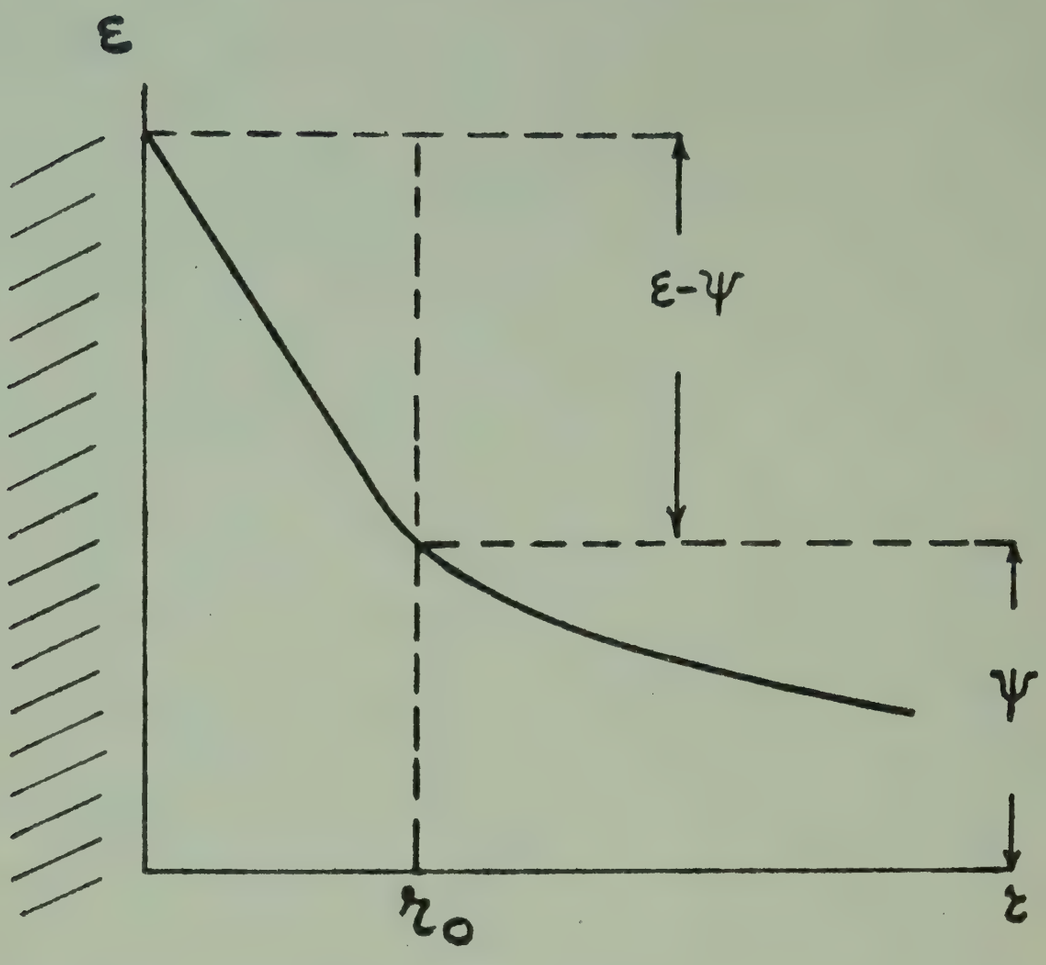

FIG. 7 — STERN'S PICTURE OF THE ELECTRICAL DOUBLE LAYER ON A METAL-SOLUTION INTERFACE. r_0 IS THE DISTANCE FROM THE METAL SURFACE AND Ψ IS THE POTENTIAL DROP IN THE DIFFUSE PART OF THE DOUBLE LAYER

the rate of discharge will be affected not by the whole value of electrode potential ϵ, but by the part of it equal to $\epsilon - \Psi$ as is shown in Fig. 8, where Ψ is the potential drop in the diffuse part of the double layer. Curve 1 corresponds to the system $M\text{-}H_{ads}$ and curves 2 and 2′ to the system $H^+\text{-}H_2O$. At the potential arbitrarily taken as zero (curve 2), the energy of activation is equal to A_d and the rate of discharge will be expressed by

$$j = KC'_{H^+} \exp\left(-\frac{A_d}{RT}\right),$$

where C'_{H+} is the surface concentration of hydrogen ions. If now the value of potential is changed from zero, the energy levels of both curves will be shifted in opposite directions. From the point of view of energy, the same result would be obtained if the curve 2 only is shifted parallel to itself (to the position of curve 2′) by the value equal to $F(\epsilon - \Psi)$.

The new value of the energy of activation (A'_d) corresponding to the cathodic potential ϵ can be shown to be:

$$A'_d = A_d - F(\epsilon - \Psi) + \alpha' F(\epsilon - \Psi),$$
$$A'_d = A_d - (1 - \alpha')F(\epsilon - \Psi).$$

Or, if $(1 - \alpha') = \alpha$,

$$A'_d = A_d - \alpha F(\epsilon - \Psi),$$

and
$$j = KC'_{H^+} \, exp \left\{ - \frac{\alpha F(\epsilon - \Psi)}{RT} \right\} \tag{12}$$

Let it be assumed that on the metal chosen as electrode the potential during the evolution of hydrogen is more negative than the null point of the metal, and that there is no pronounced specific adsorption of cations. In this case,

$$C'_{H^+} = C_{H^+} \, exp \left(- \frac{\Psi F}{RT} \right) \tag{13}$$

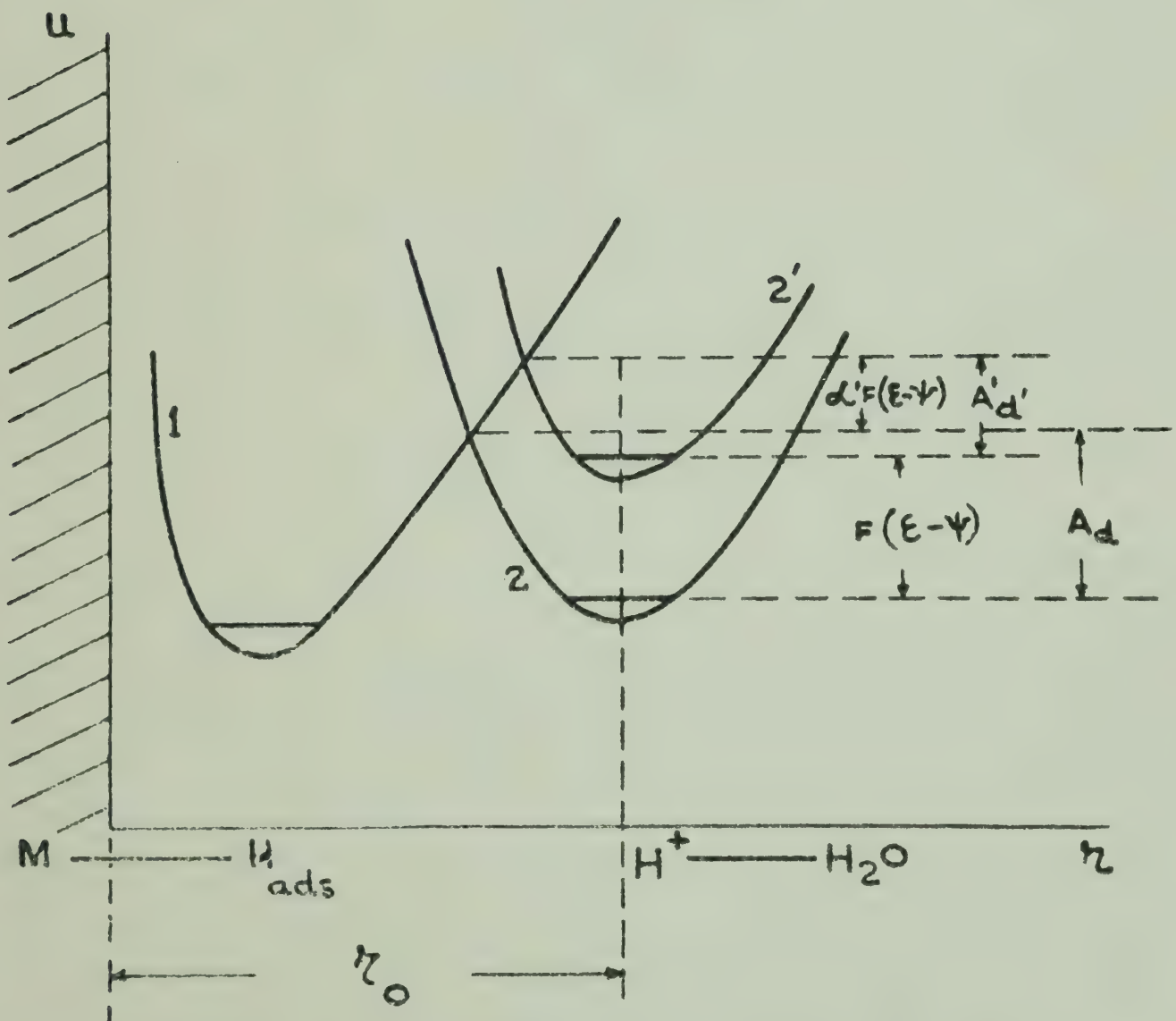

FIG. 8 — POTENTIAL ENERGY CURVES REPRESENTING THE DISCHARGE OF HYDROGEN IONS ON TO METALLIC SURFACES. THE STRUCTURE OF THE DOUBLE LAYER CORRESPONDS TO THAT GIVEN IN FIG. 7

From (12) and (13) the expression

$$\eta = const. - \left(\frac{1-\alpha}{\alpha}\right)\frac{RT}{F} lnC_{H^+} + \left(\frac{1-\alpha}{\alpha}\right)\Psi + \frac{RT}{\alpha F} lnj \qquad (14)$$

may be obtained for hydrogen overpotential.

This equation is more complicated than the empirical Tafel's formula. The latter may be considered as a particular case of (14). In concentrated solution of acids ($> 0{\cdot}1$N) or even in dilute acidic solutions when a foreign electrolyte is present in excess, the Ψ-potential is small and more or less constant. Here, instead of (14), the equation

$$\eta = const.' - \left(\frac{1-\alpha}{\alpha}\right)\frac{RT}{F} lnC_{H^+} + \frac{RT}{\alpha F} lnj \qquad (15)$$

may be written and the overpotential will be a function of H^+-ion concentration. Very often α is near 0·5 and the overpotential will be increased by 0·06 V. when the pH is increased by 1.

In the range of pure dilute acid solutions the value of Ψ is a function of C_{H^+} of the form

$$\Psi = -B + \frac{RT}{F} lnC_{H^+} \qquad (16)$$

In this case if the previous assumption concerning the value of α is held,

$$\eta = const.'' + \frac{2RT}{F} lnj \qquad (17)$$

and a change of pH will not affect the magnitude of hydrogen overpotential.

Electrochemical Groups of Metals. As will be shown below, not only the value but also the nature of hydrogen overpotential is of great importance in many of the electrochemical processes. To find the real nature of hydrogen overpotential a series of diagnostic criteria for the hydrogen evolution reaction has been given[14, 14a, 15, 16]. These criteria have been recently discussed[17*]. In this treatment, only the relation between the

*The same problem has also been discussed by Lukovtcev, P. D., in *J. phys. Chem., Moscow,* **21** (1947), 589, in connection with electrode processes where two or more stages have approximately the same rate.

heat of hydrogen adsorption* on metals and the mechanism of hydrogen evolution will be considered[19].

Taking aqueous acidified solution, the discharge of hydrogen ions on two metals (M_1 and M_2) with different values of heat of hydrogen adsorption may be represented by Fig. 9. It is seen that the energy of activation of discharge is less on the metal (M_1) with higher heat of adsorption, and it is greater on the metal (M_2) with lower heat of adsorption. At the same time, the rate of combination of adsorbed hydrogen atoms which simultaneously leads to desorption of hydrogen molecules will increase along with the decrease of heat of adsorption, if the surface concentration remains constant. If the surface concentration of hydrogen atoms does not remain constant, but increases with the heat of adsorption (as one should expect), the rate of combination may be also increased. The magnitude of this acceleration will,

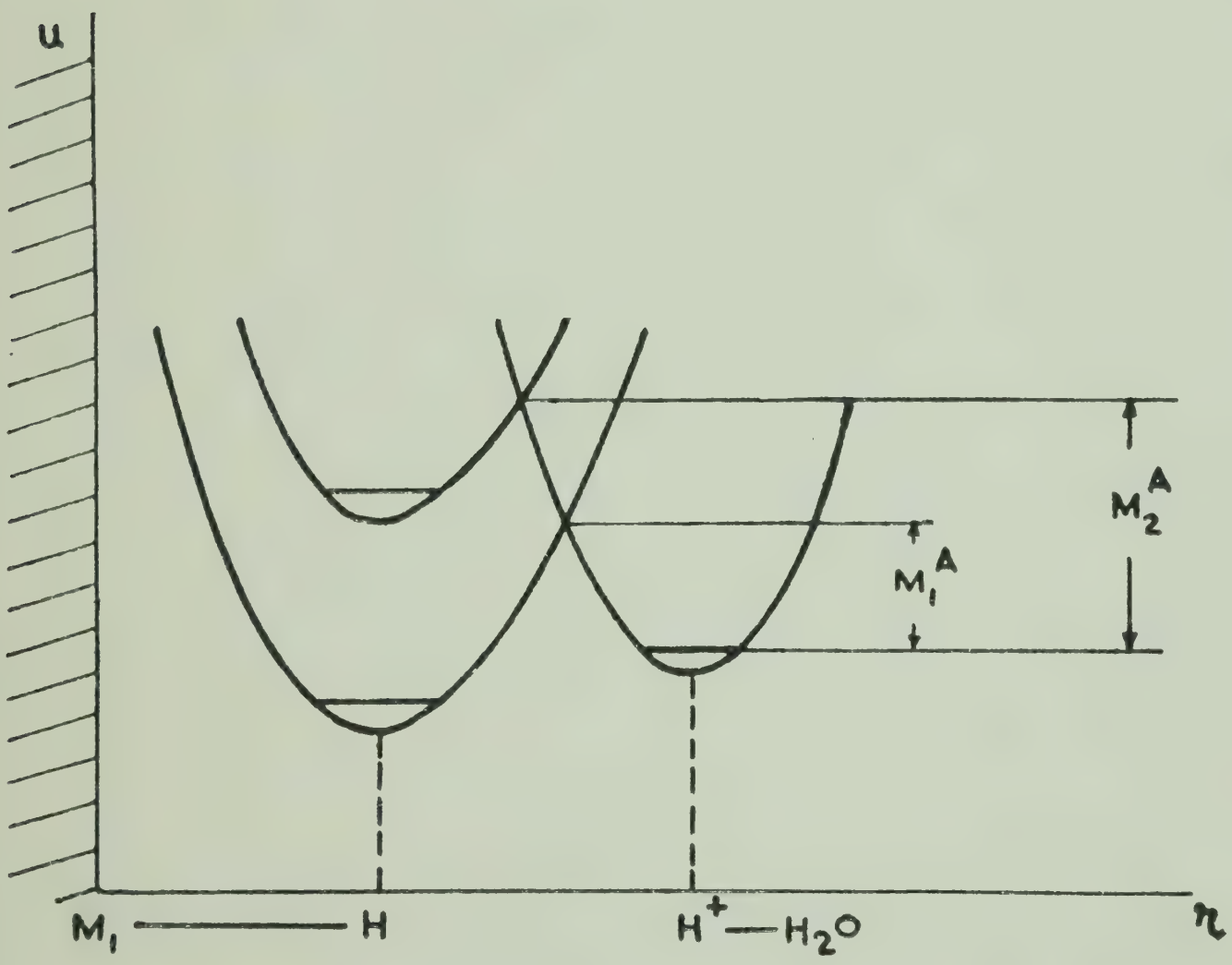

FIG. 9 — THE EFFECT OF HEAT OF HYDROGEN ADSORPTION ON THE ACTIVATION ENERGY OF DISCHARGE OF HYDROGEN IONS

*Kobozev and Nekrasov[18] have drawn the attention of electrochemists to the important role of heat of adsorption of hydrogen in cathodic evolution.

TABLE 2 — COMPARISON OF METALS OF TWO ELECTROCHEMICAL GROUPS

	Group I	Group II
Heat of adsorption of hydrogen	High	Low
Energy of activation of discharge of hydrogen ions	Low	High
Probable cause of hydrogen overpotential	Slow combination of hydrogen atoms	Slow discharge of hydrogen ions
Surface concentration of hydrogen atoms under cathodic polarization	High	Low

however, be always less than that of the discharge rate. The natural conclusion is that on metals like M_1 the combination is slow and it may cause the hydrogen overpotential, while on metals like M_2 the origin of overpotential is connected with the retarded discharge of hydrogen ions. This general conclusion is in fairly good agreement with the results obtained by applying the above-mentioned diagnostical criteria. In the following treatment, metals which behave like M_1 will be referred to as metals of the Electrochemical Group I and metals like M_2 as metals of the Electrochemical Group II. Their comparison is given in Table 2.

These two Electrochemical Groups correspond, of course, only to extreme cases in the kinetics of hydrogen evolution. There is no doubt that for certain metals the specific rates of combination and discharge are of the same order and a change of conditions (current density, composition of solution, etc.) will lead to an alteration of the mechanism of electrolytic hydrogen evolution. The evolution of hydrogen may also follow other mechanisms, as for example, the discharge of hydrogen ions on adsorbed hydrogen atoms:

$$H_3O^+ + H_{ads} \longrightarrow H_2 + H_2O$$

The experimental evidence for this so-called ' electrochemical ' mechanism is, however, still very poor at present. The detailed consideration of these and other possibilities of hydrogen evolution is, however, beyond the scope of this treatment.

CHAPTER THREE

ELECTRODEPOSITION OF METALS

Metal Overpotential Series. The electrodeposition of a metal from an aqueous solution of a simple salt of the metal normally occurs at a more negative potential (ϵ_j) than the reversible value (ϵ). The difference ($\epsilon - \epsilon_j$) is known as the metal cathodic overpotential ${}_M\eta$. The value of ${}_M\eta$ is a function of current density, temperature, composition of solution and nature of metal. In this chapter we will only consider electrodeposition of metals from solutions of their simple salts.

According to Foerster[20], metals may be arranged in a series in which the cathodic overpotential increases from left to right:

Hg, Pb, Cd, Cu, Zn, Co

Frölich and Klark[21] have found that the overpotential increases from Hg to Pd in the order: Hg, Au, Cu, Zn, Fe, Co, Ni, Pt, Pd.

Volmer[22] has given the following series of metals in the order of their overpotentials: Hg, Pb, Zn, Cd, Cu, Ag, Fe, Co, Ni.

According to Vagramyan[23] the overpotential of metals increases in the following order: Ag, Cu, Co, Fe, Ni.

On the basis of these and many other data[24-29], a general order of metallic overpotentials may be presented as follows: Hg, Ag, Pb, Tl, Cd, Bi, Sn, Cu, Zn, Co, Ni, Fe (Series I).

The overpotentials in Series I increase from Hg to the metals of the iron group. For the first five or six metals the overpotential is of the order of n mV.; for the metals in the middle of Series I, it is of the order of $n \times 10$ mV., and for Co, Ni and Fe of the order $n \times 100$ mV. Series I reveals the relationship between the value of metallic overpotentials and the nature of the metal. In certain cases two neighbouring metals may change places and the values of overpotentials can also be affected by the nature of anions[25], but as far as aqueous solutions of simple

metallic salts are concerned, Series I remains essentially the same. An interpretation of Series I will, therefore, be of great importance, both practically and theoretically.

General Picture of Metal Electrodeposition. The process of metal electrodeposition may be represented by potential energy curves (Fig. 10). The activation energy of this process would be a function of both the heat of hydration (H) and the work function of the metallic ion (Y). But this simple conception of "discharge" of metallic ions cannot explain the origin of Series I[24]. This point can be illustrated by the example of Cd and Fe which, though far removed from each other in Series I, have approximately the same values of H and Y: Cd (H), 476; Cd (Y), 432; Fe (H), 467; and Fe (Y), 430 k.cal./mole.

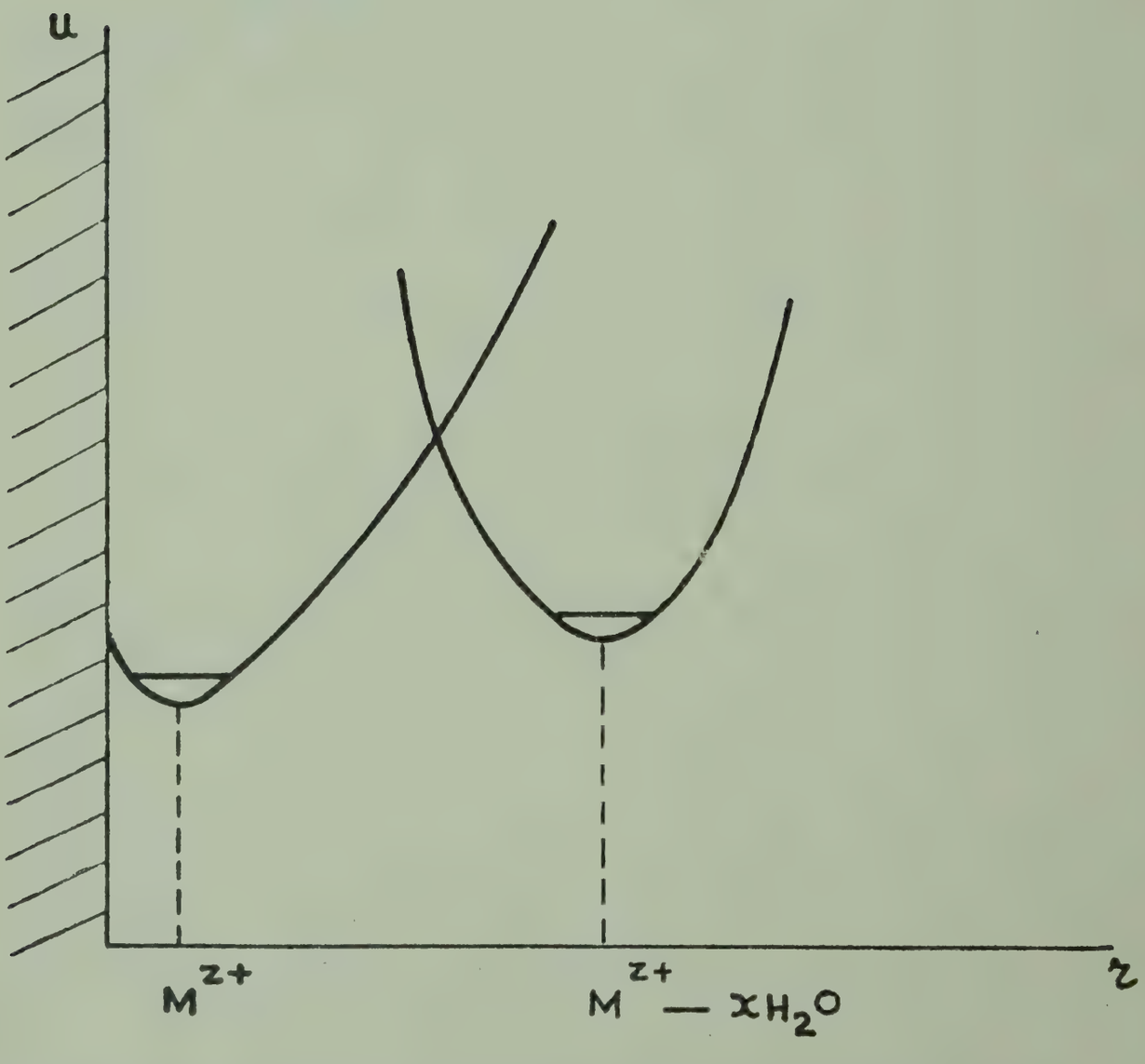

FIG. 10 — POTENTIAL ENERGY CURVES REPRESENTING THE CATHODIC DISCHARGE OF METALLIC IONS

It is well known* that the standard potential series can be derived from the values of H and Y. Since there is no physical relationship between Series I and the standard potential series, it is obvious that there will be no correlation between the magnitude of metallic overpotentials and the values of the differences $(H-Y)$[30].

Such an approach towards electrode processes based on idealized potential energy diagrams, although very helpful when applied to cathodic hydrogen evolution, cannot be accepted in its simple form in the case of metal electrodeposition. Some additional assumptions will, therefore, be necessary in order to establish the relationship between metallic overpotentials and the properties of metals and solutions (Series I).

Electronic Structure and Overpotential of Metals. Many authors believed that the overpotential of a metal is a function of the electronic configuration of ions both in the solution and metal phases[25,31,32]. This idea was developed by Lyons[33] in its most general form.

The theory of Lyons associates the overpotential of a metal with the necessity of rearranging the electronic configuration of the ion in solution into the electronic configuration of the ion in the metal lattice. The greater the difference in electronic configuration, the higher the overpotential. Lyons also suggested that metals are more easily deposited from "outer orbital" complexes (formed with the help of outer electrons) than from "inner orbital" complexes (formed with the help of the electrons from the penultimate shell).

While this theory furnishes a very promising approach to an understanding of the electrode process, it is not sufficient to derive the Series I†. Another drawback of the theory of Lyons is that the real electronic structure of many ions is not exactly known at present. The theory also does not take into account the structure of the electrical double layer at the metal-solution interface and the charge of the metal with respect to the solution. Further, several exceptions to the general rule suggested by Lyons are known. Thus, the deposition of Pt can be carried

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*Butler, J. A. V., *Trans. Faraday Soc.*, **19** (1923), 729; Gurney, R. W., *Ions in Solution* (Cambridge University Press), 1936.

†Somewhat different rules based on the polarographic behaviour of inorganic compounds have been formulated by Vlćek[34].

out in spite of the "inner orbital" nature of its complexes. Lyons tried to explain this phenomenon as being due to the high value of the energy of sublimation (112 k.cal./mole). This explanation fails, however, in the case of tungsten and molybdenum which possess still higher energies of sublimation (160 and 212 k.cal./mole respectively) but cannot be deposited from aqueous media. The high overpotential for the deposition of iron is also in contradiction to the outer orbital nature of its common tetra aqua complexes.

Effect of Secondary Phenomena on Metal Overpotential. The electrodeposition of metals occurs in many cases not on the pure surface of the metal but on the metal surface partially or completely covered with some kind of a film. In this case, the value of overpotential will not only be a function of H and Y and of the electronic structures of metallic ions, but also a function of the nature of the surface film. The presence of a surface film will normally increase the activation energy of the electrodeposition process.

It was suggested* that the difference in overpotential of various metals is a result of the different abilities of metals to form this passive film. In accordance with this, the metals of the iron group, which can be easily transformed into the passive state are at the same time very inert towards electrode processes. But it is well known that on the surface of many other metals, such as silver and lead, with a very low, if any, activation polarization, the formation of passive films takes place quite easily. The passivation process, therefore, may contribute to the overpotential, but it cannot be the decisive factor.

The second reason for the fact that it is not possible to argue only on the basis of potential energy curves and electronic structure is that metal electrodeposition is generally accompanied by the simultaneous discharge of hydrogen ions. Frölich and Klark[21] have stated that the hydrogen overvoltage series is roughly the inverse of the metallic overpotential series. They as well as some other authors[31] assumed that the cathodic hydrogen may function as a negative catalyst in metal electrodeposition. It is quite clear, however, that it is not the amount of cathodic hydrogen evolved which determines the character of the electrodeposition process. The yield of hydrogen is usually the same

*Cf. Vagramian[23] where the literature on this point is discussed.

in the electrodeposition of Zn and Fe for instance, but only in the latter case does it affect the metallic overpotential. The hindrance to the process of metal electrodeposition produced by cathodic hydrogen seems to be connected with the mechanism of hydrogen evolution on the given metal. If the combination of adsorbed hydrogen atoms is the rate-determining or slow step in hydrogen evolution, the surface concentration of hydrogen will be high and it is reasonable to expect the influence of hydrogen on the electrodeposition of the metal. But if the combination is an instantaneous process, and hydrogen overvoltage is controlled by the discharge of protons, then the surface concentration of hydrogen would be negligibly small. In this case, the effect of hydrogen on metal deposition will be insignificant. Therefore, the evolution of hydrogen ought to play a part in the electrodeposition of a metal and a correlation between the magnitude of metallic overpotential and the mechanism of hydrogen overpotential will exist[16,35].

Both these factors (passivation and adsorption of hydrogen) cannot, however, determine the order of metals in Series I, since the latter remains approximately the same when mercury is used as a cathode instead of a solid metal. For the same reason one finds it difficult to accept the theories[22] ascribing metallic overvoltage to the difficulties in formation of a metallic lattice. In some cases, however, the formation of two- and three-dimensional nuclei may be important for the electrodeposition of metals (*see below*).

φ-Potential of Metals and Metallic Overpotential. The composition of galvanic baths used normally are such that when a metal is immersed in a bath, its reversible potential does not differ very much from its standard potential. Therefore, at least the initial stage of electrolysis (and in many cases the steady state of electrodeposition also) occurs at potentials not very different from the standard reversible potentials. It was mentioned above that there is no relation between Series I and the standard potential series given in the hydrogen or in any other relative scale. At the same time, a definite relationship can be found between Series I and the series of standard potentials in the φ-scale[4]. The values of φ°-potentials tabulated in Table 3 are given in the order of increasing negative values.

TABLE 3 — SERIES II: STANDARD POTENTIALS OF METALS IN THE φ-SCALE

METAL	ϵ°	$\epsilon_{q=0}$	$\phi^\circ=\epsilon^\circ-\epsilon_{q=0}$
Hg	0·80	−0·21	1·01
Ag	0·80	−0·05	0·85
Pb	−0·13	−0·67	0·54
Tl	−0·34	−0·82	0·48
Cd	−0·40	−0·72	0·32
Cu	+0·34	0·10	0·24
Co	−0·27	−0·51	0·24
Sn	−0·14	−0·34	0·20
Zn	−0·76	−0·64	−0·12
Fe	−0·44	−0·02	−0·42
Ni	−0·23	−0·21	−0·43

The series of φ°-potentials of metals, which we may call Series II, coincides with Series I (p. 17). The only exceptions are Co and Sn which occupy different positions in Series I and II.*

This coincidence may be understood if the charge of the metal and the structure of the electrical double layer are considered to be of primary importance in the kinetics of metal electrodeposition. In this case the following explanation of Series I may be given on the basis of metal φ-potentials.

When $\varphi^\circ > 0$ the charge of the metal is positive and the solution side of the double layer will consist of anions (Fig. 4). This sheet of anions will accelerate the deposition of positively charged metallic ions. The real activation energy of " discharge " ought to be less than that expected from the corresponding values of H and Y (Fig. 10). The adsorption of anions on the metal-solution interface is a very rapid process and, therefore, this acceleration effect will prevail throughout the whole process of electrodeposition. This effect becomes more pronounced with increasing positive values of φ° and normally with increasing surface activity of anions.

When $\varphi^\circ = 0$ there will be neither acceleration nor hindrance to the process of discharge. Only in this case will the process of electrodeposition be determined by the values of H and Y.†

*These deviations may be connected either with some errors in estimation of $\epsilon_{q=0}$ values or with the effect of some secondary factors.

†On the assumption that there is no influence of secondary factors.

When $\varphi^\circ < 0$, the charge of the metal will be negative and the solution side of the double layer will be formed of cations (Fig. 6). No activation effect can be expected here. On the contrary, if foreign cations are present, they will hinder the discharge of metallic ions.

The magnitude of the increase in overpotential due to the change in the charge of the metal from positive to negative is not known exactly, but may be approximately estimated from the hydrogen overpotential data. It was found[36-39] that when metals of the Electrochemical Group II are taken as cathodes in the evolution of hydrogen, then in the region where $\epsilon_j = \epsilon_{q=0}$, a sharp change of polarization will be observed. At potentials more positive than $\epsilon_{q=0}$ (i.e. $\varphi > 0$) the overvoltage is low, while at potentials more negative than $\epsilon_{q=0}$ (i.e. $\varphi < 0$) the overvoltage is high. Normally, this difference of overvoltage is about 0·2 to 0·4 V., but in some cases it may be more than 0·6 V., as was observed for thallium amalgams[39]. The alteration of overpotential due to the change in the sign of φ-potential is very nearly equal to the change of overpotential when the electrodeposition of metals at the extremes of Series I (Hg and Ni) is considered. Therefore, the value of φ-potential seems to play an important part in establishing the metallic overpotential.

There are many experimental facts proving this hypothesis. Thus, it was found that foreign cations, and especially hydrogen ions, increase the overpotential in the electrodeposition of Ni, Zn and some other metals[40-43]. On the contrary, small anions which are surface active accelerate the process of discharge of metallic ions. It is well known that anions can be adsorbed even on a negatively charged metal surface, but their influence in this case is less pronounced than in the case of metals with $\varphi > 0$[44].

φ-Potentials of Metals and the Magnitude of Ionic Exchange Current. The anionic film present on the surface of metals with $\varphi > 0$ will accelerate not only the deposition but also the dissolution of metals. Foreign cations adsorbed on the surface of metals with $\varphi < 0$ ought to prevent not only the discharge but also the dissolution of metals. It is quite natural, therefore, to expect a correlation between φ-potentials and the ionic exchange current (i_o). If experimental data obtained by various authors for both solid metals and amalgams are taken

into account[45-58], the metals may be arranged according to decreasing values of i_o in the manner:

Hg, Ag, Tl, Pb, Cd, Sn, Bi, Cu, Zn, Fe, Co, Ni (Series III)

This series is practically identical to Series I and II; the deviations may be ascribed to the influence of different secondary factors. The magnitude of i_o increases when surface active anions are present and decreases in the presence of foreign cations[44,51,54,59,60].

All this indicates that there is a quantitative relationship between φ° and i_o. The lack of reliable and reproducible data both for φ° and i_o does not, however, permit us to establish the exact relation, but an indication of the nature of the relationship may be given. Fig. 11 represents the values of i_o obtained for mercury and for amalgams (1×10^{-3}N) plotted against the values of φ-potentials calculated from experimental data of $\epsilon_{q=0}$[6,7]. It can be seen that the ionic exchange current increases regularly with positive values of φ-potential. This justifies the suggestion that φ-potentials may be used for the estimation of i_o and vice versa.

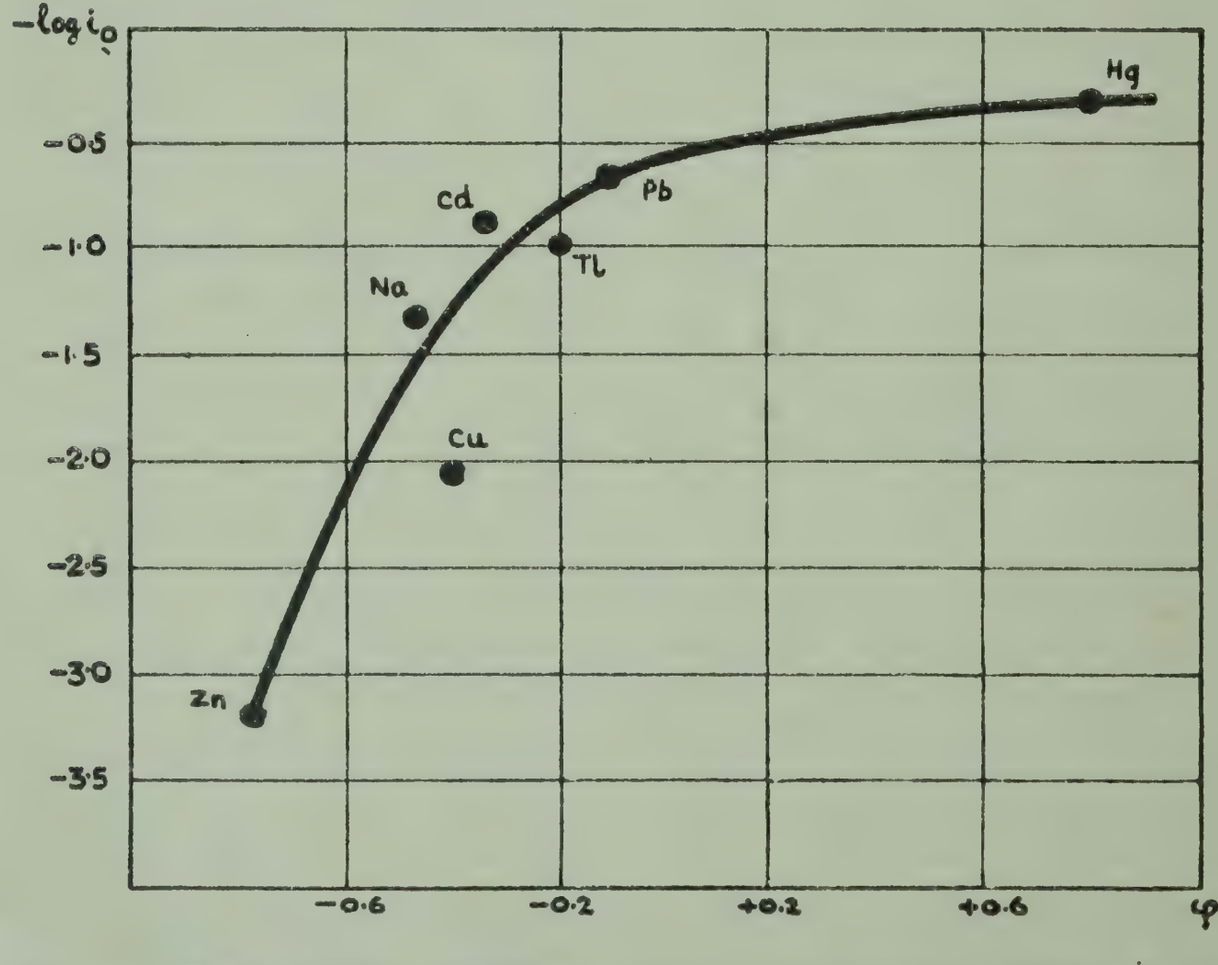


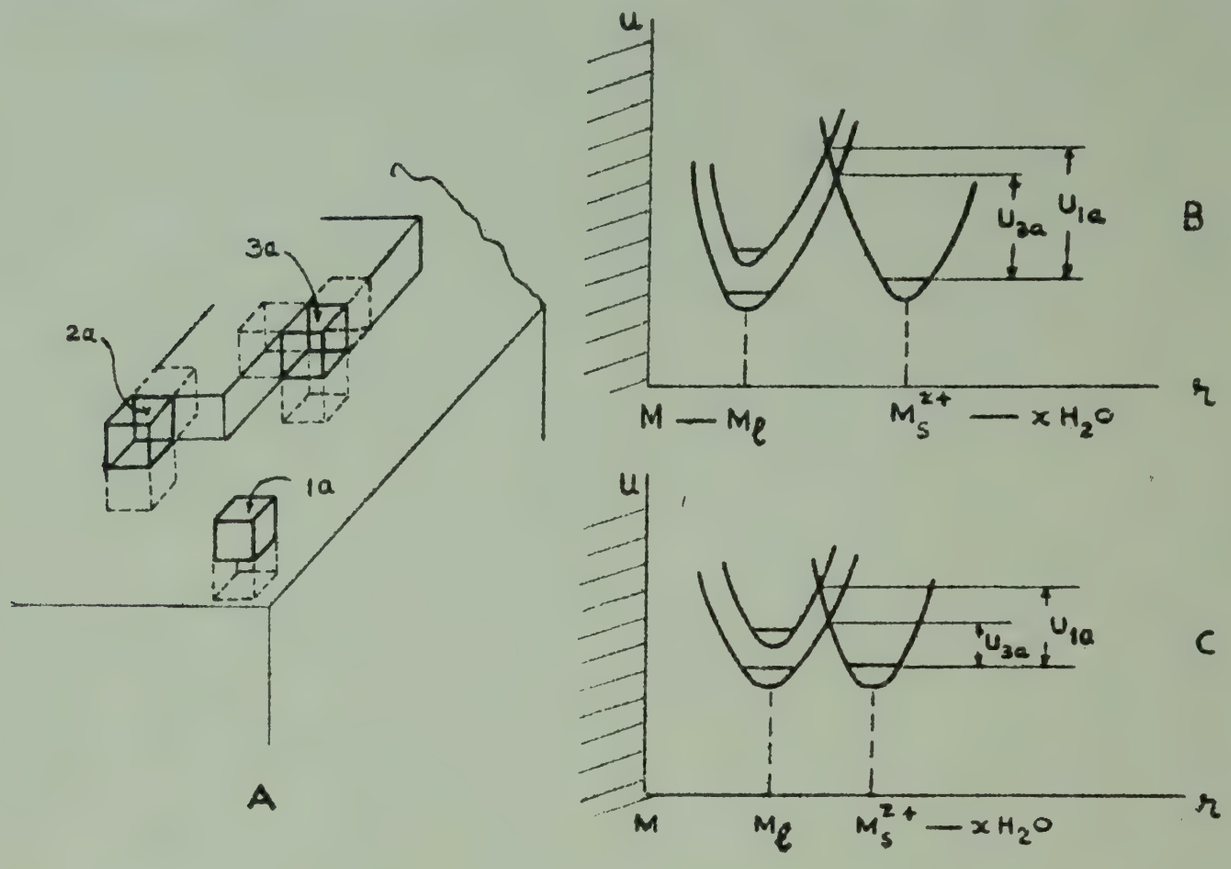
FIG. 11 — RELATIONSHIP BETWEEN THE IONIC EXCHANGE CURRENT i_o AND THE φ-POTENTIAL OF A METAL

Structure of Metal Deposits and φ°-Potentials. The electrodeposition of metals may be considered as a particular case of phase transformation*. By analogy with the transformation of a liquid phase into a solid phase, an intermediate stage consisting of the formation of nuclei of the new phase is of great importance here. The excess energy connected with this process was considered by some authors to be the cause of metallic overvoltage[61-63]. That this view is in general not correct has been shown above; but in some cases the conditions of nuclei formation may determine both the value of metallic overpotential and the structure of the deposit.

Fig. 12A shows three different positions: 1a, 2a and 3a of a new element of metallic lattice which correspond to one, two and three neighbouring elements of lattice being in contact with it. The energy of interaction depends on the number of neighbouring elements and, therefore, in the position 3a it will be approximately three times greater than in the position 1a. If the activation energy of the discharge of metallic ions is much more than the difference between the energies 3a and 1a (Fig. 12B), discharge will take place practically on all points of the metallic surface resulting in a fine crystalline deposit. But, if the energy of activation of discharge is comparable with the energy equal to 3a—1a (Fig. 12C), only a few two-dimensional nuclei will grow and a coarse crystalline deposit will be obtained.

The retardation of discharge is almost completely eliminated if the value of φ°-potential is sufficiently positive and in this case the process of electrocrystallization becomes decisive. This is actually observed for Ag, Tl and other metals with highly positive values of φ°. Their cathodic deposits obtained from solution of simple salts are normally a conglomerate of separate and rather big crystallites. Under certain conditions spiral growths are typical for silver electrodeposits and the metallic overvoltage may be estimated and compared with the energy of formation of two-dimensional nuclei. The results of such a comparison[64,65]

*The electrodeposition of metals differs from the usual process of their crystallization at least in two ways: (1) during metal electrodeposition the oversaturation can be brought about by the cathodic potential, and, therefore, overpotential may be considered as a measure of oversaturation; (2) this process occurs at a potential not equal to the reversible value, and, therefore, electrodeposition is not necessarily connected with a decrease in the potential energy. In many cases, the potential energy of the final state is higher than that of the initial state.



FIGS. 12A-C — 12A. THREE DIFFERENT POSITIONS OF A NEW ELEMENT IN THE LATTICE OF A GROWING METALLIC DEPOSIT. 12B. POTENTIAL ENERGY CURVES REPRESENTING THE DISCHARGE OF METALLIC IONS WITH ENERGY OF ACTIVATION MUCH HIGHER THAN 2a. 12C. POTENTIAL ENERGY CURVES REPRESENTING THE DISCHARGE OF METALLIC IONS WITH ENERGY OF ACTIVATION OF A VALUE COMPARABLE WITH 2a

show that in this particular case the overpotential observed is very small, and that it corresponds to the energy of formation of two-dimensional nuclei.

For metals like Fe the energy of activation for discharge is high and this process is sluggish. One of the most important reasons for this is, as was indicated above, the negative value of φ°, i.e. the hindering action of foreign cations adsorbed on the negative surface of the metal. The other plausible reason is the increased surface concentration of hydrogen atoms due to the high heat of adsorption of hydrogen and also due to a slow rate of their combination. The adsorbed hydrogen atoms normally form the negative pole of a *M-H* bond. Under certain circumstances, however, the hydrogen atoms may act as the positive pole and their action on the discharge of metallic ions is probably similar to the action of adsorbed foreign cations. The difference in energy, which corresponds to the two positions of a new element of the metallic lattice is negligibly small in comparison with the

activation energy of discharge. Hence cathodic deposits of iron and other metals with $\varphi^\circ < 0$ will be fine-crystalline. It seems, therefore, that not only the value of metallic overpotential but also the structure of cathodic deposits are connected with the sign and values of φ°.

Effect of Composition of Solution on Metal Electrodeposition and φ°-Potential. A knowledge of the φ-potential which corresponds to the conditions of metal electrodeposition makes it possible to predict the nature of particles adsorbed on the surface of a deposit. For metals with highly positive values of φ°, the overpotential up to the limiting diffusion current does not exceed several milli- or centi-volts. Therefore, the value of the φ-potential and also the charge of the metal remains positive under cathodic polarization. Further, quite contrary to the commonly held view, adsorption of anions will presumably take place on the surface of a growing electrodeposit, and the process of electrodeposition of such metals (Pb, Tl and others) will, therefore, be influenced by the nature of anions present in the solution. The influence of foreign cations may be neglected in this case. The positive value of φ-potentials of metals like Ag, Pb and others occupying the left side of Series I and II explains their insensitivity to the action of the usual inhibitors of metal electrodeposition. At the potentials remote from $\epsilon_{q=0}$ ($\varphi > 0$), the surface concentration of non-ionic compounds is low, and the surface concentration of cations is negligibly small.*

A change in the anion of a simple metallic salt may result in the alteration both of the overpotential and of the structure of the deposit. In many cases an increase of overpotential is accompanied by a decrease of the average size of crystal grains and by the formation of more uniform deposits. But for metals with $\varphi > 0$ the relationship may be quite different. Consider a part of the deposit shown in Fig. 13. The potential on the projection will be more negative than that on the hollow to the extent of $\varphi_1 - \varphi_2 = \Delta\varphi$ equal to the ohmic drop of potential through the distance l. Now, let the electrocapillary curves 1 and 2 (Fig. 14)

*The results of electrocapillary measurements obtained for mercury are used here, but the conclusions will remain true for any other metal since at equal φ-potentials the charges of all metals and the conditions of adsorption are very similar. A more detailed treatment of inhibitor action is given in Chapter V. The same approach can be utilized in the case of metal electrodeposition.

correspond to the two different anions (A_1 and A_2). It is obvious that in the presence of anions A_2 the overpotential will be less. This is because at the potentials φ_1 and φ_2 the surface concentration of anions A_2 and consequently their effect on the energy of activation for discharge of metallic ions is higher than in presence of anions A_1. At the same time, the difference in surface concentration on the two sites will be greater in the case of anions A_2 (Fig. 14). Therefore, in the presence of anions A_2 the increase in the rate of discharge in the hollow will be more pronounced as compared with that on the peaks in spite of the low

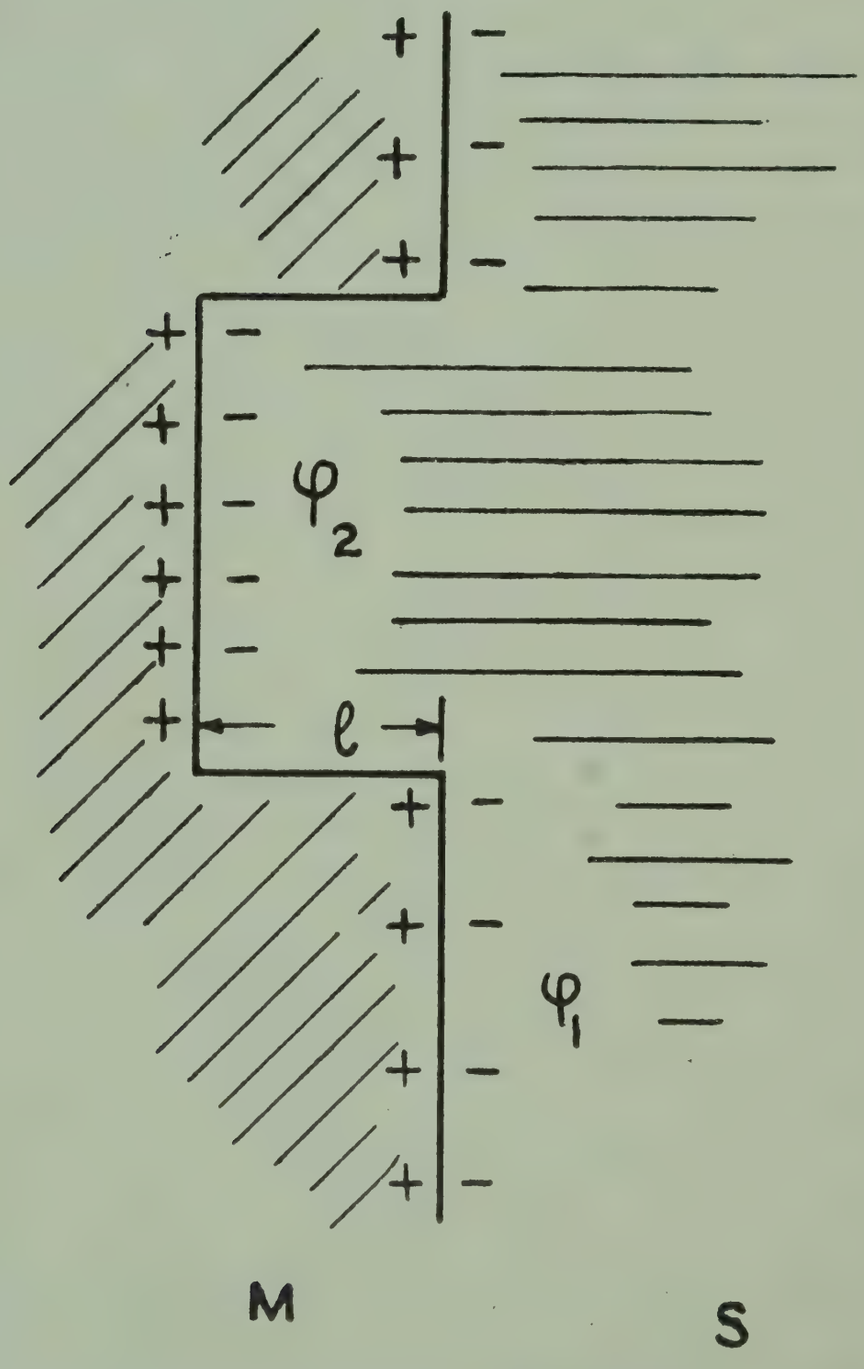


FIG. 13 — DISTRIBUTION OF CHARGES IN THE ELECTRICAL DOUBLE LAYER ON DIFFERENT PARTS OF AN ELECTROLYTIC DEPOSIT OF METAL WITH $\varphi > 0$

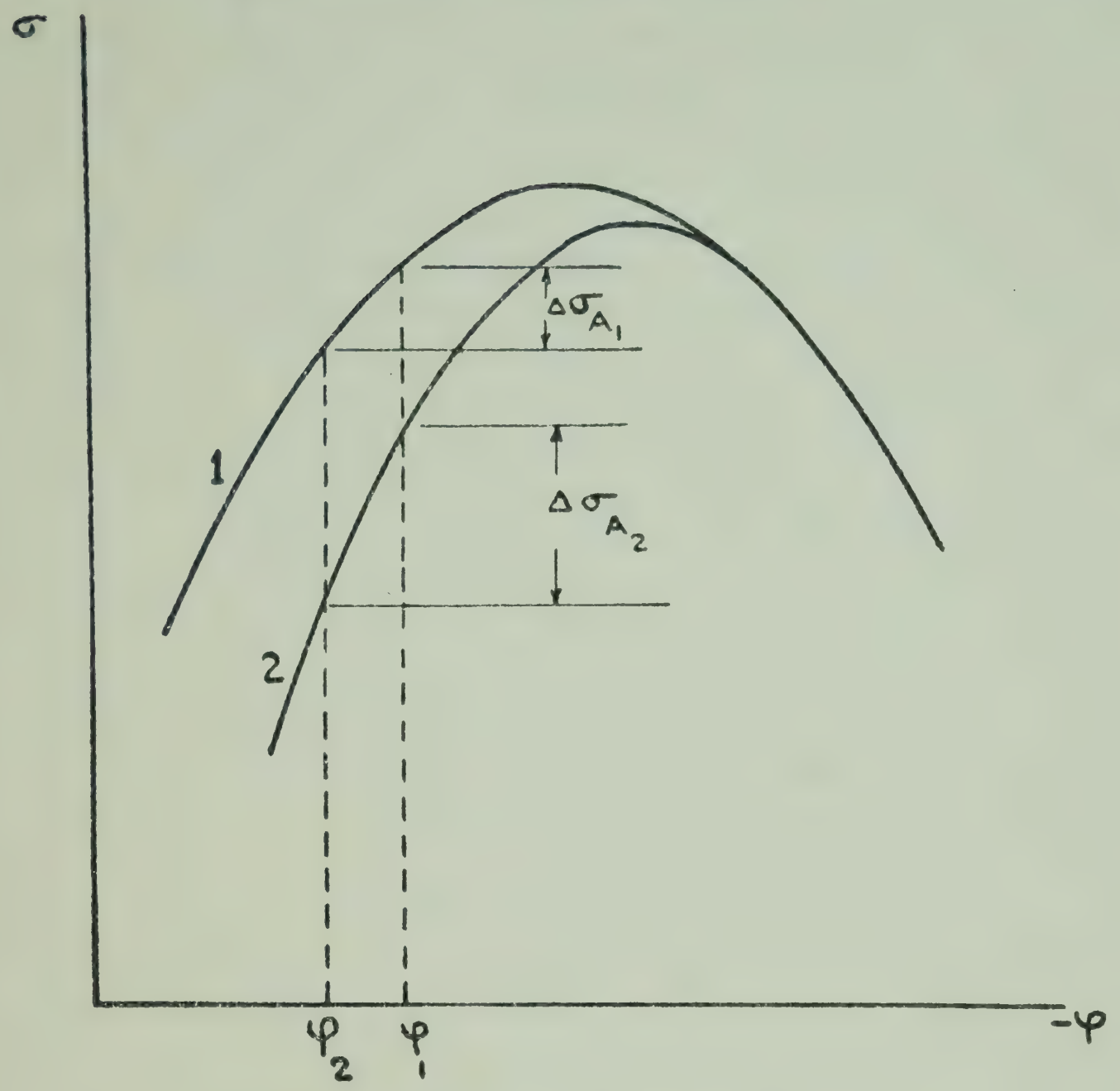


FIG. 14 — ELECTROCAPILLARY CURVES CORRESPONDING TO SALTS OF A METAL, WITH TWO DIFFERENT ANIONS A_1 (CURVE 1) AND A_2 (CURVE 2)

overpotential, and the conditions will be more favourable for the formation of a uniform deposit.

For metals with $\varphi^\circ < 0$, the solution side of the electrical double layer is formed of cations. Any foreign cations present in the solution can, therefore, play the part of inhibitors of the electrodeposition process. A decrease in pH of the solution in particular will normally result in an increase of overpotential. All cations and positively charged particles can be used here as inhibitors of electrodeposition. If the value of φ° is not too far from zero, molecular compounds will also be adsorbed on the metal surface and will hinder the process of cathodic deposition. A more detailed consideration of the influence of addition agents

on the process of electrodeposition (similar to that given for metals with $\varphi^\circ > 0$) leads to the following conclusions.

An increase of overpotential in the course of electrodeposition of metals with $\varphi^\circ < 0$ normally results in more uniform type of cathodic deposits, because the adsorption of cations as well as of many organic compounds and hence their inhibition, will be more pronounced at the peaks than at the hollows. Under certain conditions, however (when φ° is negative, and near the desorption potential of molecular or cationic inhibitors), the conditions may be similar to those under which there is an influence of inhibitors on the electrodeposition of metals with $\varphi^\circ > 0$.

Additional Remarks. It has been shown above that the value of the φ-potential, i.e. the charge of the metal with respect to the solution, and the structure of the electrical double layer are very important factors in the process of metal electrodeposition. This point of view can also be illustrated by the following example based on the papers published by Essin and Loschkarev[66] and especially by Loschkarev and his collaborators[67-71].

Loschkarev has discovered a new type of polarization which he has called "adsorption polarization". The essence of this phenomenon is that, in the presence of many organic compounds, electrodeposition of metallic ions on mercury electrodes occurs at much lower current densities than in their absence. These current densities, within certain limits, are not influenced by the value of the cathodic potential (Fig. 15). When a very negative value of potential is reached, the effect of organic compounds ceases and normal electrodeposition of metal is observed. Comparison of polarization data with results of electrocapillary and differential capacity measurements shows that organic compounds cease to act because they are desorbed from the metal-solution interface. This desorption occurs when cathodic potentials are very remote from the null point of mercury, i.e. when the φ-potential is very negative.

With the help of the φ-scale of potentials it is possible to use experimental data obtained for mercury for predicting the influence of organic compounds on the electrodeposition on solid metals.

It can be accepted that the desorption and adsorption potentials in the φ-scale will be, as a first approximation, independent

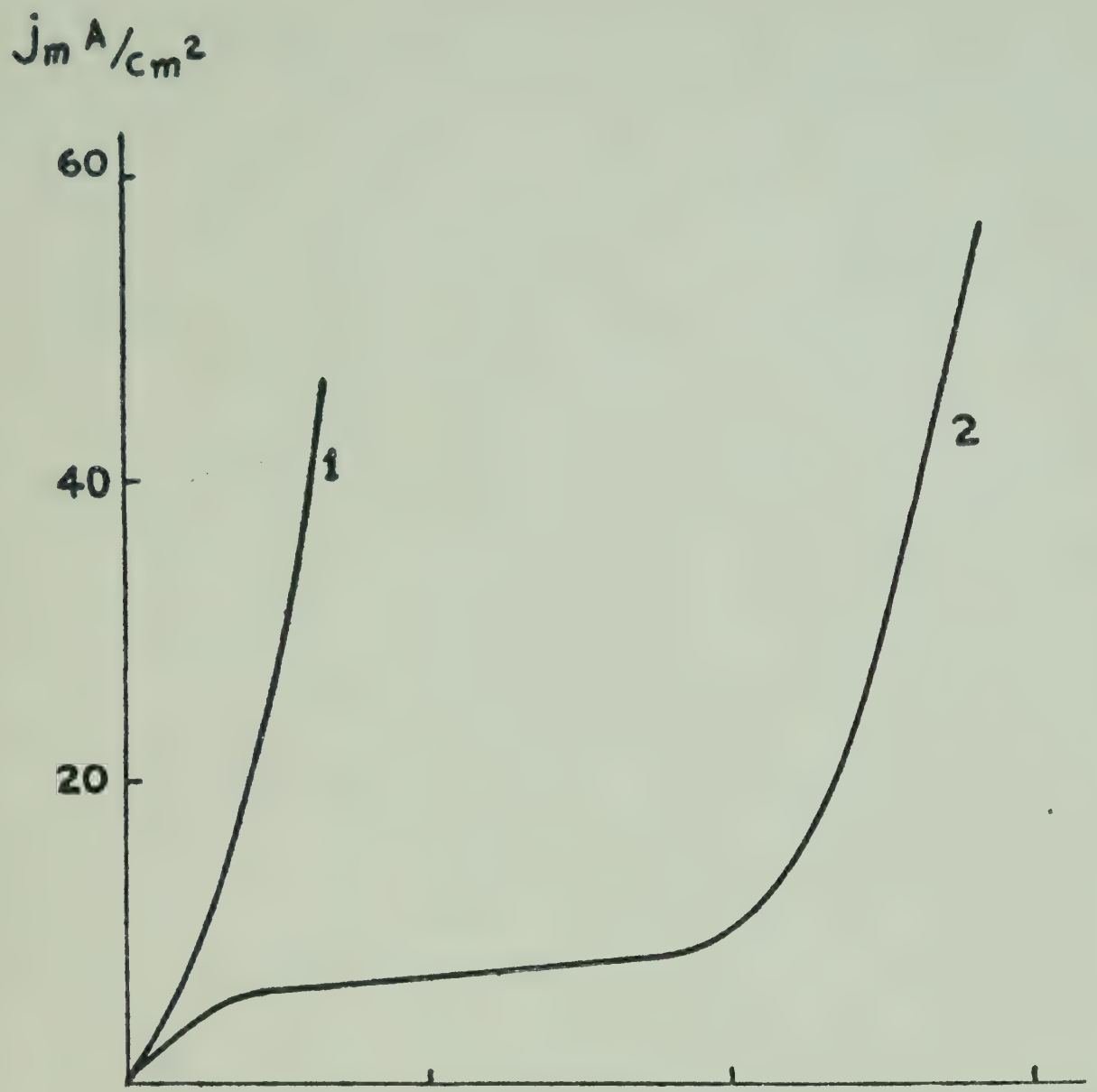


FIG. 15 — THE CHANGE OF CURRENT DENSITY DUE TO ADSORPTION POLARIZATION IN THE COURSE OF METAL DEPOSITION WITHOUT ADDITION OF ORGANIC COMPOUND (CURVE 1), AND WITH ADDITION (CURVE 2)

of the nature of the metal and will remain constant for each given compound. In contrast, they will be different for each metal if given in the ϵ-scale. Thus the adsorption of tetrabutylammonium sulphate (which has been chosen as an illustrative example) starts on the surface of mercury at a potential equal to $+0{\cdot}1$ V. in the hydrogen scale ($\epsilon_{ad} = +0{\cdot}1$ V.). The particles of the same compound are desorbed from the mercury surface at a potential equal to $-1{\cdot}2$ V. in the hydrogen scale ($\epsilon_d = -1{\cdot}2$ V.)[71]. The null point of mercury is approximately $-0{\cdot}2$ V. and the region of adsorption given in the φ-scale is located between

$$\varphi_{ad} = +0{\cdot}1 - (-0{\cdot}2) = +0{\cdot}3\,\text{V. and}\,\varphi_d = -1{\cdot}2 - (-0{\cdot}2) = -1{\cdot}0\,\text{V.}$$

These values of adsorption and desorption potentials given in the φ-scale correspond to different ε-potentials as is given below for several metals:

Metal	Ag	Pb	Fe	Zn
$\epsilon_{q=0}$	+0·05	−0·67	−0·02	−0·64
ϵ_{ad}	+0·35	−0·37	−0·34	+0·28
ϵ_{d}	−0·95	−1·67	−1·02	−1·64
ϵ°	+0·80	−0·13	−0·44	−0·76

The process of electrodeposition of silver and lead from many solutions of simple salts occurs at potentials that do not differ much from normal potentials, i.e. beyond the region of adsorption of tetrabutylammonium and many other cations. This means that the electrodeposition of these two metals cannot be influenced by tetrabutylammonium sulphate because it is not adsorbed on the surface of the above metals during their cathodic deposition.

In the electrodeposition of iron and zinc, however, the cathodic potentials coincide with the region of adsorption of tetrabutylammonium ions (as well as of many other cations) and the latter will affect the process of electrocrystallization. Moreover, its effect will be observed at more negative values of ε-potentials as compared with the electrodeposition of the same metals on the mercury electrode.

These conclusions are in conformity with the inhibiting action of organic compounds on the electrodeposition of the above metals. The agreement between theory and experiment accentuates the importance of φ-potentials in the process of electrocrystallization. At the same time, it must be noted that the value of the φ-potential is not the only factor which determines the course of metal electrodeposition. It is probable that in several cases other factors are predominant and prevail over the influence of φ-potential. These factors, as indicated by many authors[23,72,73] are the formation of surface films and the hydrodynamic conditions obtaining during electrodeposition.

The various cases of deviation from the results that may be expected on the basis of φ-potential arguments have been discussed previously[4]. We shall consider here only the deviations which result from an alteration of the nature of sorption of anions.*

*A comprehensive treatment of electrochemical reactions involving the participation of anions has been given recently[74].

It has been assumed that the physical adsorption of anions will always accelerate the discharge of metallic ions. But in some cases, the bond between anions and metals does not correspond to simple physical adsorption. There may be, for instance, chemical interaction between metal atoms and the anions, leading to the formation of a chemical complex on the metal surface. In this case a decrease of the rate of discharge may be observed instead of an acceleration[75,76]. Further, different types of sorption of anions may take place on different sites of the same cathodic deposit, which results in additional non-homogeneity of the crystalline structure. If anions of large dimensions and of small valency are added to the solution, their adsorption on the metal surface may lead to increasing metallic overpotential, as the acceleration caused by the increased surface concentration of negatively charged particles may happen to be less than the additional hindrance due to the larger part of the metal surface being covered by anions.

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CHAPTER FOUR

ELECTROREDUCTION

Electroreduction and Hydrogen Overpotential. The most common viewpoint regarding the influence of cathodic potential on the electroreduction process may be stated as follows: the greater the hydrogen overpotential, the more efficient will be the electrode in an electrochemical reduction process. This means that metals of higher hydrogen overpotential ought to be always the best cathodes, and that for a given metal the efficiency of electroreduction will increase normally with overpotential.

Thus, it was stated in the well-known text-book by Creighton[77] that " The magnitude of the cathode potential is a measure of its reducing power and this is greater the higher the cathode potential ".

To explain the exceptions to this rule some unknown catalytic properties of metals were invoked. At present so many exceptions have been established that the rule itself has doubtful validity[78].

The simple relation between hydrogen overpotential and the reducing power of a cathode may be expected to hold only when both the mechanism of hydrogen evolution and the mechanism of the electroreduction process remain the same for all metals and at all values of electrode potential. But, the mechanism of hydrogen evolution is not the same for different metals and probably for different values of electrode potential (Chapter II). Equal values of cathodic potentials or equal values of hydrogen overpotential for different metals will not, therefore, correspond to similar reduction conditions. This indicates that as far as the electroreduction process is concerned, not only the value but also the nature of hydrogen overpotential ought to be taken into account.

Types of Electroreduction[16,19,79]. Earlier (Chapter III) it was shown that the heat of adsorption of hydrogen (qH) is high

and the rate of combination of adsorbed hydrogen atoms is low on metals of Electrochemical Group I. Therefore, the concentration of hydrogen atoms on the surface of these metals during the course of their cathodic polarization ought to be very high. Under these circumstances the electroreduction of inorganic and organic compounds by means of adsorbed hydrogen atoms is very plausible.

On metals with a low value of qH (Hg, Pb and other metals of Electrochemical Group II) whose overpotential is determined by slow discharge of hydrogen ions, only a negligibly small part of the surface is covered by hydrogen atoms. The surface concentration of hydrogen atoms is extremely low, and reduction by adsorbed hydrogen atoms is, therefore, unlikely. But a new possibility arises, namely reduction by means of discharging hydrogen ions. The reason for this possibility can be seen from Fig. 9 (Chapter II). When a metal of the Electrochemical Group II is taken as a cathode, the activation energy of discharge of hydrogen ions is high, and the latter will acquire a substantial part of the energy of hydration before they are discharged. These partially dehydrated ions can react with organic substances especially if the activation energy of electroreduction is less than that of discharge. An adsorbed particle can act as a "bridge" with the help of which an electron can combine with a hydrogen ion. This possible mechanism is excluded in the case of cathodes of Group I because the hydrogen ions discharged on these are almost completely hydrated and hence remain inactive.

On both the groups of electrodes, in addition to their specific reduction processes, reduction by electrons may also take place.

In accordance with the above, three possible causes of overpotential of electroreduction reactions may be postulated:

1. Slow transfer of electrons (one or two) to adsorbed organic particles.
2. Slow addition of activated hydrogen ions (one or two) to adsorbed organic particles.
3. Slow reaction between adsorbed hydrogen atoms (one or two) and adsorbed organic particles.

Electroreduction by Electrons[16]. The current density j is distributed between two competing processes: discharge of hydrogen ions (j_1), and electroreduction of organic compounds (j_2):

$$j = j_1 + j_2 \qquad (18)$$

If the discharge of hydrogen ions is the rate-determining step of hydrogen evolution then*

$$j_1 = kC'_{H^+} \exp\left\{-\frac{\alpha_1 F \epsilon_{Rj}}{RT}\right\} \tag{19}$$

where, C'_{H^+} is the surface concentration of hydrogen ions. In most of the cases C'_{H^+} may be taken as equal to the volume concentration C'_{H^+} and

$$j_1 = k_1 C'_{H^+} \exp\left\{-\frac{\alpha_1 F \epsilon_{Rj}}{RT}\right\} \tag{20}$$

The rate of reduction assuming that the subsequent addition of hydrogen ions occurs without hindrance may be given as

$$j_2 = k_2 C'_R \exp\left\{-\frac{\alpha_2 F \epsilon_{Rj}}{RT}\right\} \tag{21}$$

where C'_R is the surface concentration of organic compounds.

It follows from (18), (20) and (21) that

$$j = k_1 C_{H^+} \exp\left\{-\frac{\alpha_1 F \epsilon_{Rj}}{RT}\right\} + k_2 C'_R \exp\left\{-\frac{\alpha_2 F \epsilon_{Rj}}{RT}\right\} \tag{22}$$

Very often $\alpha_1 = \alpha_2 = \alpha$ and the following expression for ϵ_{Rj} may be written as

$$\epsilon_{Rj} = -\frac{RT}{\alpha F} \ln j + \frac{RT}{\alpha F} \ln (k_1 C_{H^+} + k_2 C'_R) \tag{23}$$

or

$$\epsilon_{Rj} = +\frac{RT}{\alpha F} \ln k_1 C_{H^+} - \frac{RT}{\alpha F} \ln j + \frac{RT}{\alpha F} \ln\left(1 + \frac{k_2}{k_1} \frac{C'_R}{C_{H^+}}\right) \tag{24}$$

Let the value of " depolarization " be determined as under

$$\Delta\epsilon = \epsilon_{Rj} - \epsilon_j \tag{25}$$

where ϵ_j is the cathode potential corresponding to the evolution of hydrogen at a current density equal to j from the same solution, but in the absence of organic compounds†

$$\epsilon_j = a' + \frac{RT}{\alpha F} \ln C_{H^+} - \frac{RT}{\alpha F} \ln j \tag{26}$$

---

*The rate of hydrogen evolution may be determined by some other process and consequently a different expression for j_1 will be used in this case.

†Hydrogen overpotential can be influenced by organic compounds. This factor may also be taken into account[80].

Substitution of ϵ_{Rj} by (23) and ϵ_j by (26) in (25) results in

$$\Delta\epsilon = a'' + \frac{RT}{\alpha F} ln \left\{ 1 + \frac{k_2}{k_1} \frac{C'_R}{C_{H^+}} \right\} \tag{27}$$

The determination of the value of polarization which corresponds to the electroreduction process involves difficulties because most of the redox processes are irreversible. But the formula (28) may be taken as a first approximation to be the real expression for the equilibrium potential.

$$\epsilon_R = const. + \frac{RT}{\alpha F} ln(C_R C_{H^+}) \tag{28}$$

The redox polarization will be equal to

$$\eta_R = \epsilon_R - \epsilon_{Rj} = const. + \frac{RT}{\alpha F} lnj - \frac{RT}{\alpha F} ln \left\{ \frac{k_1 C_{H^+}}{c_R^a C_{H^+}^a} + \frac{k_2 C'_R}{c_R^a C_{H^+}^a} \right\} \tag{29}$$

All the above equations may be simplified if the yield of the reduction process is near 1. In such a case equations (30), (31) and (32) may be written instead of (23), (27) and (29).

$$\epsilon_{Rj} = -\frac{RT}{\alpha F} lnj + \frac{RT}{\alpha F} ln\, k_2 C'_R \tag{30}$$

$$\Delta\epsilon = const. + \frac{RT}{\alpha F} ln \left(\frac{k_2 C'_R}{k_1 C_{H^+}} \right) \tag{31}$$

$$\eta_R = const. + \frac{RT}{\alpha F} lnj + \frac{RT}{\alpha F} ln \left(\frac{k_2 C'_R}{c_R^a C_{H^+}^a} \right) \tag{32}$$

Electroreduction by Activated Hydrogen Ions[16]. A similar method of consideration may be applied to this case and if $j_2 = j$, the following expressions will be obtained:

$$\epsilon_{Rj} = const. - \frac{RT}{\alpha F} lnj + \frac{RT}{\alpha F} lnC'_R + \frac{RT}{\alpha F} lnC_{H^+} \tag{33}$$

$$\Delta\epsilon = const. + \frac{RT}{\alpha F} lnC'_R \tag{34}$$

$$\eta_R = const. + \frac{RT}{\alpha F} lnj - \frac{RT}{\alpha F} lnC'_R - \frac{RT}{F} \left(\frac{1-\alpha}{\alpha} \right) lnC_{H^+} \tag{35}$$

Electroreduction by Adsorbed Hydrogen Atoms[16]. On the basis of assumptions similar to those for electroreduction by

electron and by activated hydrogen ions, the following series of equations may be derived:

$$\epsilon_{Rj} = const. + \frac{RT}{F} lnC_{H^+} - \frac{RT}{2\beta F} lnj + \frac{RT}{2\beta F} lnC'_R \qquad (36)$$

$$\Delta\epsilon = const. + \frac{RT}{2\beta F} lnC_R \qquad (37)$$

$$\eta_R = const. + \frac{RT}{2\beta F} \frac{lnj}{C_R} \qquad (38)$$

where β is the Freundlich constant.

It may be noted that the above equations are of a general nature and the equations which have been derived previously by other authors[81-86] can be obtained as special cases.

Other Possible Ways of Electroreduction. Besides the possibilities considered above, several other probable mechanisms for the electroreduction process have been suggested. Thus, it was assumed that the electroreduction reaction may occur by means of free hydrogen atoms and activated hydrogen molecules emitted from the electrode surface under cathodic polarization[18,87,88]. The formation of these active species was attributed to the decreased value of the heat of adsorption of hydrogen (q'H) on the surface of the electrode as compared with the average value of the heat of reversible hydrogen adsorption from the vapour phase qH. During the course of the electrolytic evolution of hydrogen, whereas hydrogen atoms can be formed at any point of the cathode surface, adsorption of hydrogen atoms from the vapour phase takes place mainly on those sites with higher values of heat of adsorption. It may be mentioned here that reduction by free hydrogen atoms seems to be rather improbable because of their very low concentration even at the highest values of hydrogen overpotential. We must add, however, that the main points of this theory of electroreduction are subjects of discussion[89-93].

The hypothesis put forward by some authors concerning electroreduction through the agency of metallic ions has not received any experimental proof so far.

Experimental Confirmation of Different Mechanisms of Electroreduction on Various Metals. The nature of the reducing agents on various electrodes may be found with the help

of the equations given in preceding sections. Thus, it has been shown that addition of activated hydrogen is the slowest stage in the reduction of nitrobenzene[94] and acetone[95] on a mercury cathode. The process of the reduction of oxygen[96,97] on mercury and silver cathodes is determined by the rate of electron transfer to the adsorbed molecule. But when platinum cathodes are used instead of mercury, the rate of reduction of nitrobenzene and oxygen is determined by the velocity of reaction with adsorbed hydrogen atoms[98]; acetone under these conditions is not reduced. Electroreduction of oxalic acid on mercury takes place through activated hydrogen ions[99] or electrons[100], this step being sluggish.

A further confirmation of the idea that the nature of the reducing agents on electrodes of metals of Electrochemical Groups I and II are different is the fact that the action of various electrodes towards the electroreduction of organic compounds is very specific. This point is illustrated in Tables 4 and 5, from which it can be seen that the electroreduction of non-polar groups and bonds takes place more easily on electrodes like Pt and Ni from Group I (reducing agents — adsorbed hydrogen atoms and electrons) and the reduction of polar groups and bonds on electrodes like Hg and Pb from Group II (reducing agents — activated hydrogen ions and electrons).

Electroreduction and the Null Points of Metals. The different mechanism of hydrogen evolution on various cathodes is not the only reason for the lack of a simple relation between the cathodic potential of a metal and its reducing power. Though in some cases, the electroreduction process may be the result of a mere collision of organic particles with the electrode, adsorption should normally be an inevitable step in electroreduction. The rate and direction of an electroreduction reaction ought to be, therefore, a function of the surface concentration of organic or inorganic compounds[102].

The same value of overvoltage or of cathodic potential in the hydrogen scale does not correspond to the same surface concentration of reducible compounds, because the surface concentration is determined by the value of the φ-potential of the electrode. Since each metal possesses its own value of null point, equal values of cathodic potentials in the ϵ-scale do not give equal values in the φ-scale.

This can be illustrated by the following example: let the process of reduction of a non-ionic organic compound take place at the potential ϵ_{Rj} which has the same value (−1·0 V.) for three metals Ag, Hg, and Pb. Since all these metals belong to Electrochemical Group II, not only will the values of cathodic potential be equal, but the mechanism of the hydrogen evolution

TABLE 4 — SPECIFIC REDUCTION OF ORGANIC COMPOUNDS ON VARIOUS CATHODES[19,79]

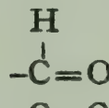
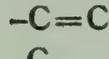
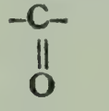
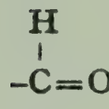
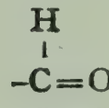
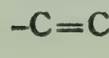
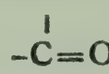
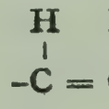
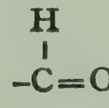
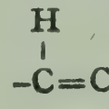
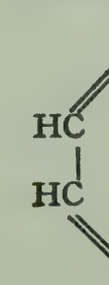
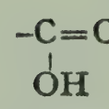
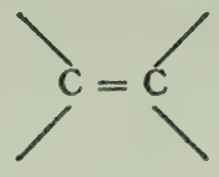
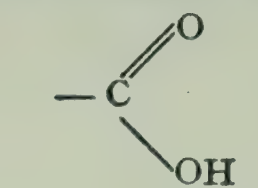
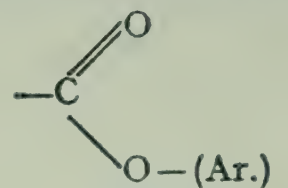
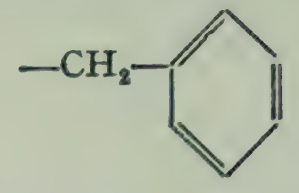
Compound	Reducible group or bond	Efficiency of reduction		Product of reduction
		Pt, Ni	Hg, Pb	
Acetaldehyde		−	+	Ethyl alcohol
Acetylene		+	−	Ethylene, Ethane
Acetone		−	+	Isopropyl alcohol propane, pinacol
Acetophenone		−	+	Benzyl alcohol, Acetopinacol
Benzophenone		−	+	Benzopinacol
Vinyl acetylene		+	−	Divinyl
Methyl propylketone		−	+	Butane
Oleinic acid		+	−	Stearic acid
Salicylic aldehyde		−	+	Salicylic alcohol
Sorbic acid		+	−	Dihydro acid
Phenol		+	−	Cyclohexanol
Oxalic acid		−	+	Glyoxalic acid, glycolic acid

TABLE 5 — EFFECT OF CATHODE ON REDUCTION OF VARIOUS GROUPS IN ORGANIC COMPOUNDS

Compound	Group:										
	Cathode:	Pb	Pt-pt	Pb	Pt-pt	Pb	Pt-pt	Pb	Pt-pt	Pb	Pt-pt
		−	+			+	−				
		−	+			+	−				
		−	$+_2$	+	$+_1$	−	−				
		−	$+_1$			+	−	−	$+_1$		
		−	$+_2$	+	$+_1$	−	−	−	$+_2$		

\+ and − indicate reducibility and non-reducibility respectively, $+_1$ and $+_2$ give the order of reducibility.
Pt-pt indicates here a platinum black electrode.

reaction will also be the same. Nevertheless, the conditions of electroreduction on all of the three metals will be very different, because the value of the reduction potential given in the φ-scale, φ_{Rj}, will not be the same. In the case of silver, it is $-1{\cdot}0-(+0{\cdot}05) = -1{\cdot}05$ V.; mercury, $-1{\cdot}0-(-0{\cdot}2) = -0{\cdot}8$ V.; and lead, $-1{\cdot}0-(-0{\cdot}67) = -0{\cdot}33$ V. A comparison of these values with Fig. 16 shows that the surface concentration is different for each of the three cathodes, and, therefore, the efficiency of reduction will not be identical although it is carried out at the same values of ϵ-potential.*

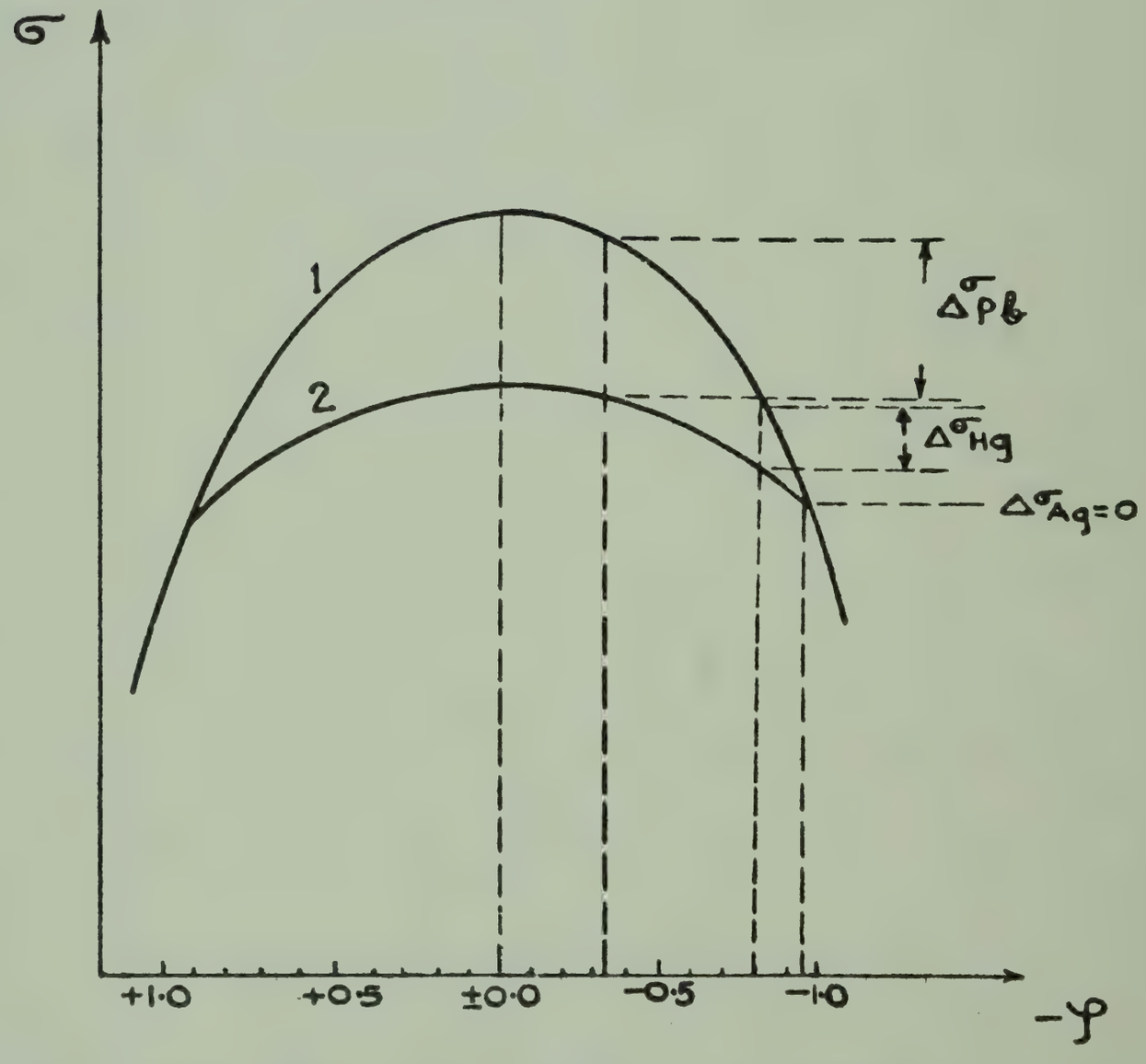


FIG. 16 — THE EFFECT OF A MOLECULAR ORGANIC COMPOUND ON THE ELECTROCAPILLARY CURVE: WITHOUT ORGANIC COMPOUND (CURVE 1), WITH ORGANIC COMPOUND (CURVE 2)

*The electroreduction of anions and cations can be treated in a similar manner.

On the basis of the above arguments, the following principles have been suggested:

1. The electroreduction of non-ionic organic compounds occurs with high efficiency when the reduction potential is not very far from the null point of electrode used for the process. At cathodic potentials which are far removed from the null point of the metal, a cessation of electroreduction may be expected[19,79,102].

2. The nearer the reduction potential is to the null point of the metal, the more favourable are the conditions for the formation of bimolecular reduction products[1,2,19,79].

In accordance with these principles, it has been found that the electroreduction of different nitro compounds occurs at values near the null point of the metal[103]. Oxalic acid is better reduced on electrodes with negative values of $\epsilon_{q=0}$[39,104]. In case of the reduction of phenylhydroxylamine on a platinum cathode a decrease in efficiency has been observed with an increasing negative value of the φ_{Rj}-potential[105], but the true "desorption limiting current" was first established by the electroreduction of anions[74,106-111]. It was found that in the current-potential curves obtained on various metals, at potentials slightly more negative than the corresponding null point, a sharp decrease of current is observed. This decrease of current is not due to diffusion because the value of the current is much lower than the limiting current density already reached for this compound. It is also not a phenomenon of "adsorption polarization" discovered by Loshkarev since no organic addition agents are present in the solution. It follows from the relation between the potential at which the sudden break of currents occurs and the null point of the metal (Fig. 17) that this is a true "desorption limiting current".

The cessation of the reduction of anions at negative φ-potential values was attributed to the repulsive forces between the anions and the negatively charged surface of the metal resulting in an extremely low surface concentration of reducible particles. Similar ideas[112,113] were employed to interpret the polarization curves obtained for the systems

$$Fe^{+++}/Fe^{++},\ Tl^{+++}/Tl^{+},\ Ce^{++++}/Ce^{+++},$$

$$V^{+++++}/V^{++++},\ Mo^{++++++}/Mo^{+++++}$$

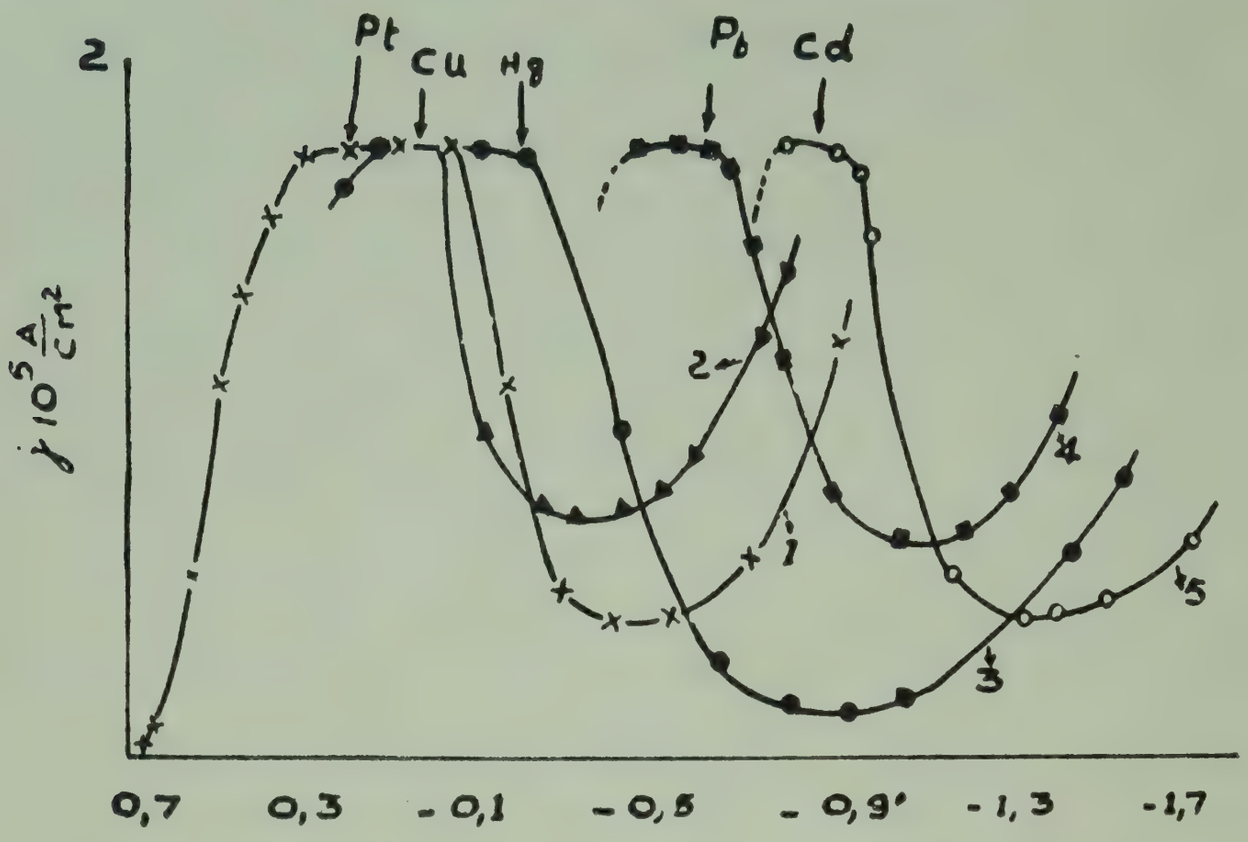


FIG. 17 — RELATIONSHIP BETWEEN CURRENT DENSITY AND POTENTIAL IN 10^{-3}N $K_2S_2O_8 + 10^{-3}$N Na_2SO_4 ON Pt, Cu, Hg, Pb and Cd CATHODES (curves 1, 2, 3, 4 and 5 respectively). ARROWS INDICATE THE PROBABLE VALUES OF $\epsilon_{q=0}$

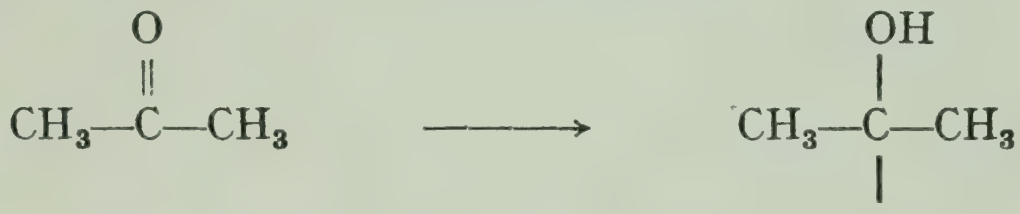
All the facts given above indicate that when the equations for the kinetics of the electroreduction process are derived, the change of surface concentration of particles being reduced ought to be taken into account. The type of functional relationship between the surface concentration of molecular organic compounds and the potential has been discussed by Frumkin[114] and Butler[115], but a further generalization of their results is desirable.

Besides the occurrence of a "desorption" limiting current density, the influence of the value of the null point of a metal may also result in a sudden change of its reducing power at a potential equal to its null point. If the molecules of the reducible organic compound are of polar nature, then, in the region of the null point, when the sign of the charge of the metal is reversed, one should expect an alteration in the orientation of the organic molecules, and hence a change in the efficiency of reduction. In addition to this, when the metals of Electrochemical Group II are used as cathodes, the region of potentials containing the null point of the metals corresponds to a rearrangement

of the solution side of the electrical double layer and hence to a sudden change in hydrogen overvoltage. The distribution of current between the two possible cathodic processes as well as the yield from the electroreduction reaction will, therefore, undergo a sudden change.

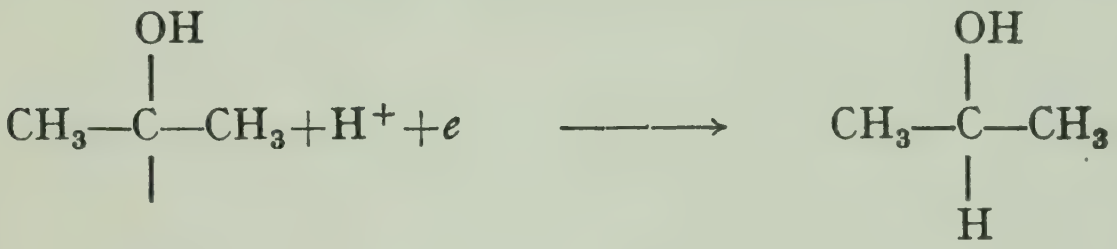
In many cases the cathodic reduction of organic compounds may result in bimolecular products or in hydrodimers[116]. Very often these hydrodimers are of more economic value than the simple products of reduction. The role of the null point of metals in processes of this kind can be illustrated by the example of the reduction of acetone (I).

The first stage of electroreduction of (I) leads, very probably, to the formation of the free radical (II):



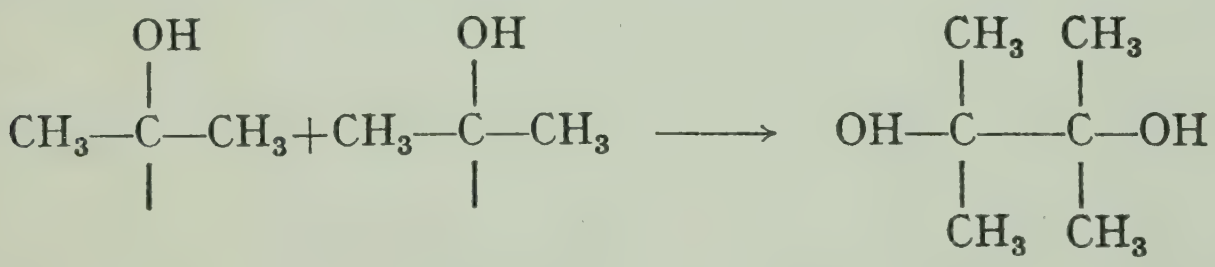
I II

The future of (II) depends on the character of its next collision. If it collides with a hydrogen atom or with a proton and electron, isopropyl alcohol will be the final product of reduction:



II

But if it collides with another free radical, the formation of pinacol (III) will be possible as under:



II II III

It is obvious that the conditions necessary for the second type of process are (i) high surface concentration of (II), and (ii) low concentration of the reducing agent. The first of these

conditions implies that the surface concentration of (I) ought to be also high. This occurs when the cathodic potential is near the null point of the metal ($\varphi_R = \epsilon_R - \epsilon_{q=0} = 0$). The second condition means that the current density should not be too high.

From this point of view it is possible to decide which of the metals used as cathodes in organic electrosynthesis — Pt, Ni, Ag, Cu, Zn, Hg or Pb — are most suitable for obtaining the pinacol in acid solutions by the electrochemical method. For solving this problem it is essential to know the reduction potential of acetone and the null points of the above-mentioned metals. The reduction potential of acetone in acid solutions is about −0·7 to −0·8 V. in the hydrogen scale[95]. The corresponding values of $\epsilon_{q=0}$ and φ_R are given in Table 6.

It follows from Table 6 that the best results can be expected with Pb and Zn electrodes. This conclusion agrees well with the experimental data of different authors[117,118]. It seems also that the strong reducing action of sodium amalgams and the high yield of pinacol, which may be obtained by means of these amalgams, are connected with the highly negative values of their null points.

The negative value of the null point is not the only reason for the increased reducibility of organic compounds when amalgams are taken instead of mercury. Sodium amalgams are normally used in alkaline solutions where the state of organic compounds is different from that in acid solutions. Thus it was shown that in alkaline solution, acetone is present in a molecular state which possesses a greater surface activity than the form in

TABLE 6 — NULL POINTS AND CATHODIC POTENTIALS OF METALS

	Metals						
	Pt	Ni	Ag	Cu	Zn	Hg	Pb
Null points ($\epsilon_{q=0}$)	+0·25	+0·21	−0·05	+0·10	−0·64	−0·19	−0·67
Cathodic potentials ($\varphi_R = \epsilon_R - \epsilon_{q=0}$)	−1·05	−1·01	−0·75	−0·90	−0·16	−0·61	−0·13

which it is present in acid solution[119]. In alkaline solutions the keto-enolic tautomeric equilibrium is shifted to the enolic form which can reasonably be identified with the surface active form of acetone.*

The state of organic compounds plays an important part not only in this particular case of reduction of acetone but also in many other reactions of organic electroreduction[121-124].

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*The assumption made by Wilson & Wilson[120] that acetone exists in alkaline solution in the form of cation $[(CH_3)_2CO.H]+$ has not been confirmed[119].

CHAPTER FIVE

ELECTROCHEMICAL CORROSION OF METALS

General Picture. Corrosion of metals may be defined as a spontaneous, destructive process which occurs on the surface of a metal as a result of its interaction with chemical agents present in the environment.

Corrosion normally leads to the formation of chemical compounds very similar to the compounds in which metals are found in their natural state (oxides, sulphides, carbonates, etc.). The energy spent by mankind to obtain pure metals from their ores and minerals is released in the process of corrosion. Therefore, corrosion is a spontaneous process which does not require any external source of energy for its occurrence.

The attack of chemical agents always takes place at the interface between the metal and its surroundings. Corrosion, therefore, is a surface process in which adsorption phenomena are of great importance.

There are two fundamental types of corrosion: chemical and electrochemical. Chemical corrosion is said to occur when the reagents are atoms and molecules and when there is no exchange of charges between the metal and its surroundings. It is a characteristic of electrochemical corrosion that the reagents are normally ions and electrons, and that the interchange of charges between metal and the environment is a necessary condition. As a result of this interchange, a potential difference is established on the metal/environment interface. This potential is known as the corrosion potential ϵ_c of the metal. Normally, ϵ_c is not equal to the reversible potential ϵ of the same metal under the given conditions. The difference between ϵ and ϵ_c as well as the difference between the equilibria of metal-solution systems and the process of corrosion may be better understood by making the following comparison[3,125].

(a) *Equilibrium State of Metal-solution System*

(i) The potential of a metal does not change with time.

(ii) This value ϵ of the potential corresponds to the reversible potential of the metal, and if the activity or concentration of its ions are known, ϵ may be calculated with the help of the Nernst formula.

(iii) ϵ is of such a value that the only possible reactions are those of dissolution and discharge of ions corresponding to the metal being used as an electrode.

(iv) Therefore, the same species and the same amount of ions are crossing the metal-solution boundary in opposite directions. If the currents corresponding to the amount of ions discharged or formed per second on unit areas of metal are denoted by $\overleftarrow{j_1}$ and $\overrightarrow{j_1}$ respectively, the following equation is true for the equilibrium state:

$$\overleftarrow{j_1} = \overrightarrow{j_1} = j_o \qquad (40)$$

where j_o is the reversible ionic exchange current density.

(v) The chemical nature and weight of the electrode do not vary with time ($\Delta m = 0$).

(vi) The composition of the solution remains constant ($\Delta C = 0$).

(b) *Steady Corrosion Process*

(i) The potential of the metal does not vary significantly with time, and can be considered as a constant.

(ii) The value of the potential ϵ_c is, in general, not equal to the reversible potential of the metal and, therefore, cannot be calculated with the help of the Nernst formula.

(iii) ϵ_c is of such a value that, besides the passage of metallic ions into solution and their discharge from solution, at least one other cathodic electrochemical process will take place (evolution of hydrogen, reduction of oxygen or some other inorganic or organic compound, deposition of more noble metal).

(iv) Not only the metallic but also some other charged particles, for example, hydrogen ions, are going, therefore, through the boundary between the metal

and solution. ϵ_c will then be constant if the total quantity of charge crossing the boundary in one direction is equal to the total quantity of charge crossing the boundary in the opposite direction:

$$\overleftarrow{j_1} + \overleftarrow{j_2} = \overrightarrow{j_1} + \overrightarrow{j_2} \tag{41}$$

where $\overleftarrow{j_2}$ and $\overrightarrow{j_2}$ are the current densities corresponding to the discharge and ionization of hydrogen respectively.

The rate of corrosion will be given by j_c as under

$$j_c = \overrightarrow{j_1} - \overleftarrow{j_1} = \overleftarrow{j_2} - \overrightarrow{j_2} \tag{42}$$

(v) The weight and in some cases the chemical nature of the electrode may change in the course of corrosion ($\Delta m \neq 0$).

(vi) The composition of the solution may also change to a certain extent ($\Delta C \neq 0$) although in many cases the alternation is not very pronounced.

Homogeneous and Heterogeneous Types of Electrochemical Corrosion. The above considerations remain true irrespective of the actual mechanism of corrosion. Let the dissolution of a highly pure and uniform sample of some electronegative metal (Zn, for example) be considered. All points of the surface of this metal are taken as energetically equivalent and the potential of the metal in contact with the solution of $p\mathrm{H} = p\mathrm{H}x$ is equal to ϵ_c. Since zinc is not found in nature in the metallic state, the process of its dissolution ought to be expected and the rate of corrosion may be calculated. The hydrogen reversible potential under the given conditions will be equal to

$$\epsilon_H = -\frac{RT}{0{\cdot}43F} pH_x \tag{43}$$

The hydrogen overvoltage on zinc in this solution may be represented as

$$_{Zn}\eta_H = {}_H\epsilon - \epsilon_c = a + b \log j \tag{44}$$

and the rate of hydrogen evolution

$$j = \overleftarrow{j_2} - \overrightarrow{j_2} \tag{45}$$

is at the same time the measure of the corrosion rate

$$j = j_c = \overleftarrow{j_2} - \overrightarrow{j_2} = \overrightarrow{j_1} - \overleftarrow{j_1} \tag{46}$$

If the values of pH, ϵ_c and the Tafel constants are known, the rate of corrosion in units of current may be found. In general, when the corrosion of a pure uniform metal is considered and the rates of each of the four processes are given as functions of potential, both the rate of corrosion and the corrosion potential may be determined by solving equation (41). All the processes, the rates of which are included in equation (41), occur independently at any point of the metal surface; the process of corrosion does not involve spatially divided anodic and cathodic zones.

In many cases equation (41) may be simplified, hence some of the terms may be neglected. For instance, if the ionic exchange current of the metal is large and greater than the hydrogen exchange current, the corrosion potential will be approximately equal to the reversible potential of the metal in the same solution and will be determined by the concentration of metallic ions and not by the pH of solution. If, in addition, this potential is negative, the rate of hydrogen ionization may be neglected. The ϵ_c potential may then be calculated here by the Nernst formula and the rate of corrosion by Tafel's equation. This simplified method of calculation is applicable as far as the decomposition of sodium and many other amalgams are concerned.

Another special case is obtained when the rate of exchange of metal ions between the metal and the solution is small as compared with the exchange current for hydrogen. Then, the potential of this corroding metal will be similar to the hydrogen electrode potential and will depend not on the concentration of metallic ions but on the pH of the solution. In estimating ϵ_c, the terms $\vec{j}_1$ and $\overleftarrow{j}_1$ may be neglected. The behaviour of iron within a certain range of pH corresponds to this special extreme case.

An estimation of the corrosion potential and the corrosion rate may also be made with the help of polarization curves — anodic and cathodic — obtained on the same sample of metal. The ordinate of the intersection of these curves will correspond to the value of the corrosion potential and the abscissa to the rate of corrosion (Fig. 18).

The above view of electrochemical corrosion is known as the theory of homogeneous electrochemical corrosion. The idea

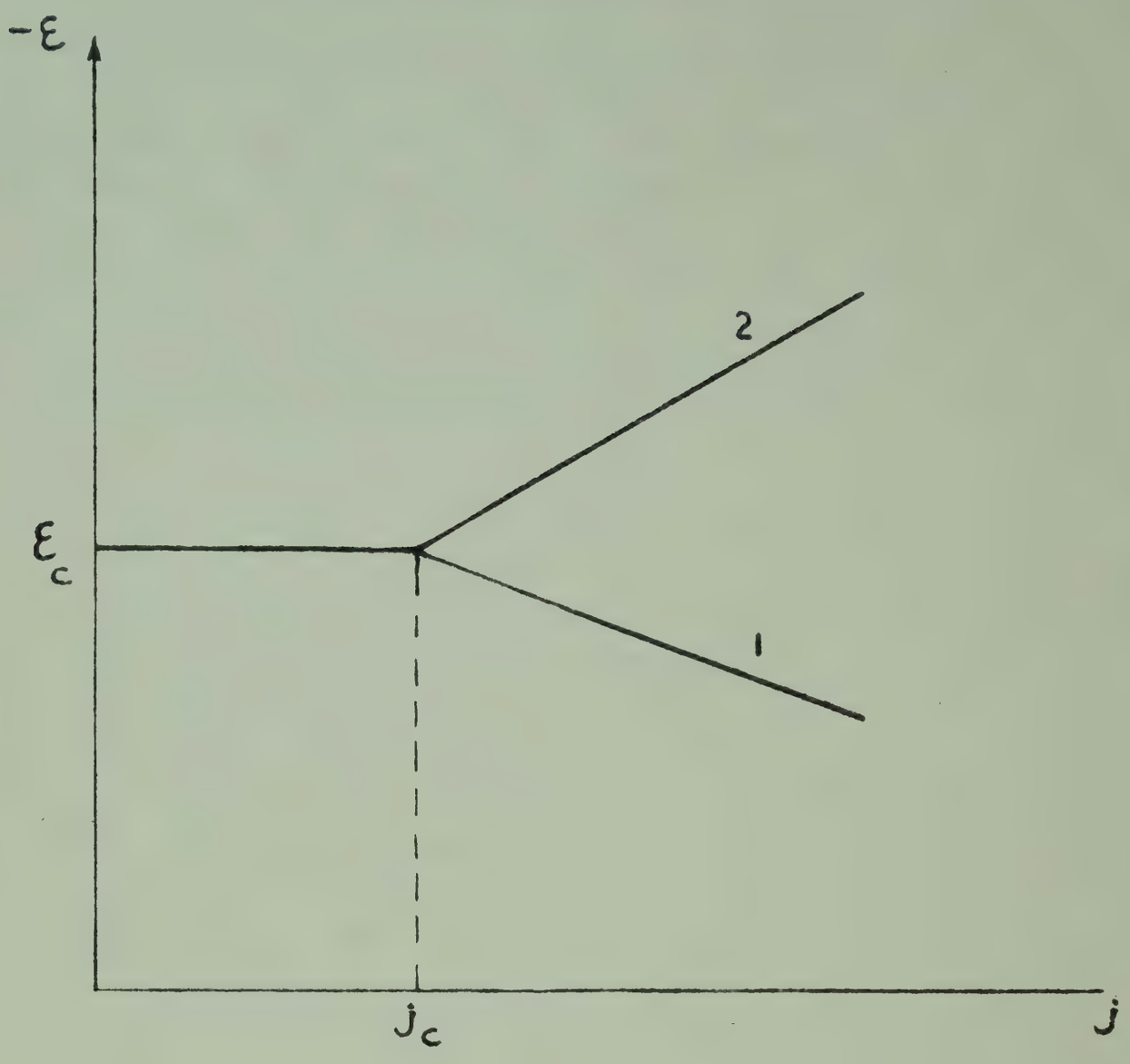

FIG. 18 — POLARIZATION CURVES REPRESENTING THE PROCESS OF HOMOGENEOUS ELECTROCHEMICAL CORROSION: (1) ANODIC DISSOLUTION OF METAL; (2) CATHODIC EVOLUTION OF HYDROGEN

of this type of corrosion was given first by Frumkin[126,127] and the foundation of its theory was elaborated by Wagner and Traud[128] and other authors[129-131]. The homogeneous theory of corrosion proved to be very useful and at present many successful applications of this theory are known[132-134].

Let us now consider the case where the metal is not pure and uniform, but contains some inclusions, for example, inclusions of a more noble metal. The corrosion of zinc in acid solution will be taken as an illustrative example. The change in the rate of corrosion brought about by inclusions will depend on the nature of the inclusions and their relative amount. Cadmium is one of the common inclusions in zinc. In the electrochemical series, cadmium is more positive than zinc ($_{Cd}\epsilon^{\circ} = -0{\cdot}40$ V., $_{Zn}\epsilon^{\circ} =$

—0·76V.) and those parts of the metal surface occupied by Cd will behave as cathodes with respect to those parts occupied by Zn. The value of ϵ_c as compared with the reversible potential of hydrogen is highly negative, and it is possible to neglect the rate of hydrogen ionization. The rate of hydrogen evolution is different on Cd and Zn as under:

$$_{Zn}\eta_H = -1{\cdot}24 - 0{\cdot}12 \log {}_{Zn}j_H$$
$$_{Cd}\eta_H = -1{\cdot}40 - 0{\cdot}12 \log {}_{Cd}j_H$$

The overpotential of hydrogen is greater on Cd than on Zn, the difference being 0·16 V. Hence, the ratio of the rates of hydrogen evolution on these two metals at the same potential will be equal to

$$\frac{_{Cd}j_H}{_{Zn}j_H} = 10^{-0{\cdot}16/0{\cdot}12} = 10^{-1{\cdot}33}$$

If the Cd-content is 1 per cent, the rate of evolution of hydrogen (j) on unit area of the corroding metal is given by

$$j = 0{\cdot}99\,{}_{Zn}j_H + 0{\cdot}01\,{}_{Cd}j_H = 0{\cdot}99 j_{in} + 10^{-1{\cdot}33}.\ 10^{-2}\ j_{in}$$
$$= 0{\cdot}99_{in} + 0{\cdot}00082_{in} = 0{\cdot}991\ j_{in} \simeq j_{in}$$

where $j_{in} = {}_{Zn}j_H$ is the initial rate of hydrogen evolution (on the surface of pure Zn). If the content of Cd is increased to 10 per cent, then

$$j = 0{\cdot}90 j_{in} + 10^{-1{\cdot}33}.\ 10^{-1} j_{in} = 0{\cdot}908 j_{in}$$

It may be concluded, therefore, that in the presence of noble metals having a higher hydrogen overpotential, the rate of corrosion of a metal will not be increased. On the contrary, a certain decrease of corrosion may be expected.*

Silver is also a probable inclusion in commercial zinc. In this case

$$_{Ag}\eta_H = -0{\cdot}95 - 0{\cdot}12 \log_{Ag} j_H,$$
$$_{Zn}\eta_H = -1{\cdot}27 - 0{\cdot}12 \log_{Zn} j_H$$

and

$$\frac{_{Ag}j_H}{_{Zn}j_H} = 10^{\left(+\frac{0{\cdot}29}{0{\cdot}12}\right)} = 10^{2{\cdot}4}$$

*The rate of corrosion also will be decreased, hence a certain part of the surface will be inactive both to cathodic and especially, to anodic processes.

If the sample of zinc contains 1 per cent of silver, the rate of evolution of hydrogen on this commercial metal is equal to

$$j = 0{\cdot}99_{Zn}j_H + 0{\cdot}01_{Ag}j_H = 0{\cdot}99\,j_{in} + 10^{2{\cdot}4}.\,10^{-2}\,j_{in} = 0{\cdot}99\,j_{in} + 2{\cdot}51\,j_{in} = 3{\cdot}50\,j_{in}$$

This means that the presence of 1 per cent of silver (which has a lower hydrogen overpotential than zinc) will accelerate the process of corrosion by a factor of 3·5. Though the silver inclusions account for 72 per cent of the hydrogen evolved, the remaining 28 per cent of the hydrogen ions will be discharged on the zinc. In this case, while the silver inclusions play the role of cathodes in the corroding system, zinc behaves both as an anode and as a cathode, but with a predominant anodic function. If the relative amount of silver is increased to 10 per cent or if instead of silver some other metal with still lower hydrogen overpotential is present as an inclusion, then it is possible to neglect the cathodic function of Zn. Only in this case will the corrosion of the metal sample occur entirely due to the action of microgalvanic couples. In fact, if 10 per cent of silver or 1 per cent of iron ($_{Fe}\eta_H = -0{\cdot}70 - 0{\cdot}12\ log_{Fe}j_H$) were present, the relative amount of hydrogen evolved on the surface of the inclusions would be equal to 96·5 and 99·9 per cent* respectively.

For this heterogeneous type of corrosion, Evans, Hoar and others suggested[135] corrosion diagrams of the type illustrated in Fig. 19. In the diagrams it is assumed that the initial (reversible) potentials corresponding to both anodic (dissolution of metal) and cathodic (evolution of hydrogen) processes are known, and that the polarization is a linear function of the current. Such a diagram is very helpful for a qualitative consideration of a corrosion process and a modification may also be used when a number of inclusions both of metallic and non-metallic origin are present[136,137]. For a quantitative estimation of the corrosion rate, the polarization curves are normally obtained on two different electrodes, i.e. on the basic metal and on the inclusion metal, and their relative areas ought to be known. In some cases, the results obtained will be different from the actual rate of corro-

*The percentage of hydrogen actually evolved here will be less because iron is not present in zinc in the form of a metal but normally in the form of a certain intermetallic compound with higher value of hydrogen overpotential.

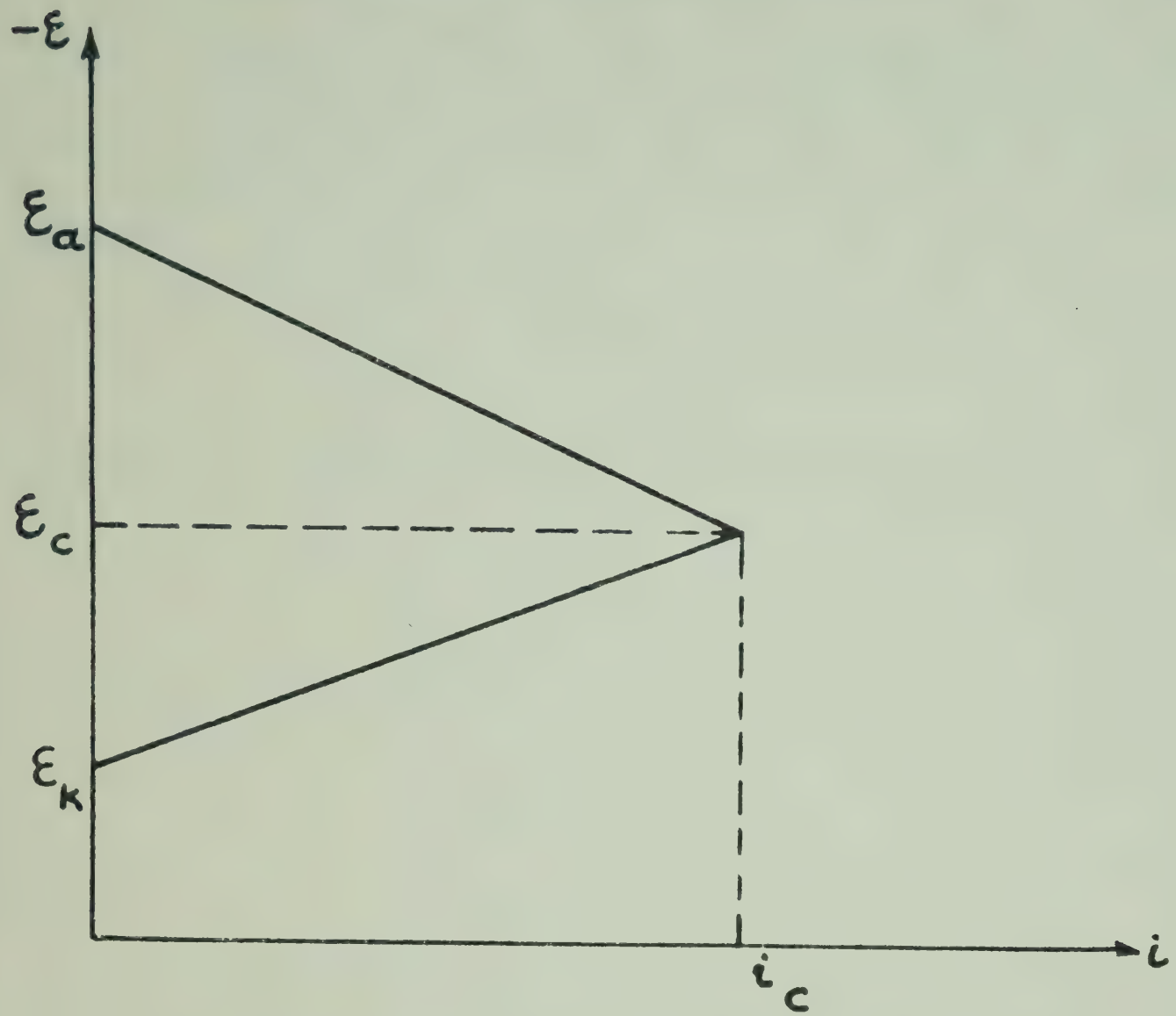

FIG. 19 — THE EVANS CORROSION DIAGRAM

sion since the evolution of hydrogen may also take place on the basic metal itself (*see above*).

In the case of purely heterogeneous electrochemical corrosion, the rate of this process may be calculated with the help of polarization curves obtained again on the same sample of metal. The part of the surface occupied by an inclusion is of no importance here because the rate of corrosion is normally related to the unit surface area of the whole metal. The study of the corrosion of commercial metals may, therefore, be carried out with the help of polarization curves taken on the same sample of metal[3]. From the above argument, it is clear that almost in all the cases the true mechanism of corrosion is a combination of both homogeneous and heterogeneous processes.

Effect of *p*H on the Corrosion Process. If the rate of a corrosion process involving hydrogen evolution is determined by the kinetics of the corresponding electrochemical reactions, the influence of *p*H must be expected. This effect will depend[3,138]

on the mechanism of hydrogen overpotential, as may be shown by the following example:

Let us again consider the case when all the terms in equation (41) may be neglected with the exception of the rate of metal dissolution ($\vec{j_1}$) and the rate of hydrogen evolution ($\overleftarrow{j_2}$). Then, the rate of corrosion will be equal to

$$j_c = \vec{j_1} = \overleftarrow{j_2}$$

and the value of the corrosion potential ϵ_c may be calculated from the equation

$$\vec{j_1} = \overleftarrow{j_2},$$

if the nature of both processes is known.

It may be assumed that for both of them the equations based on Tafel relation

$$\eta_a = a_a + b_a \log j_a \tag{47}$$

and

$$\eta_k = a_k + b_k \log j_k \tag{48}$$

are true.

The value of overpotential may be found from the corrosion potential and the reversible potentials of anodic (ϵ_a) and cathodic processes (ϵ_k) as indicated by equations below:

$$\epsilon_c = \epsilon_a + \eta_a \tag{49}$$

and

$$\epsilon_c = \epsilon_k - \eta_k \tag{50}$$

From (47), (48), (49) and (50), it follows that

$$\epsilon_c = \epsilon_a + a_a + b_a \log j_a \tag{51}$$

and

$$\epsilon_c = \epsilon_k - a_k + b_k \log j_k \tag{52}$$

If the corroding metal has an uniform and equipotential surface*, then

$$j_a = j_k = j_c$$

and

$$\log j_c = -\frac{a_a + a_k}{b_a + b_k} + \frac{\epsilon_k - \epsilon_a}{b_a + b_k} \tag{53}$$

---

*If the metal contains a certain inclusion occupying a fraction of the surface area equal to S, an additional term $\frac{-1}{b_a + b_k} \log (1-S)^{b_a} S^{b_k}$ will appear in equation (53).

When the kinetics of hydrogen evolution is determined by the rate of combination of adsorbed hydrogen atoms, the hydrogen overpotential and hence the value of a_k will not depend on the pH of the solution. The value of ϵ_k will be the only term affected by pH.

$$\epsilon_k = -\frac{RT}{0{\cdot}43F} p\mathrm{H} = -b_o p\mathrm{H}$$

Using this expression for E_K, the following equation may be written:

$$log\ j_c = const. - \frac{b_o}{b_a + b_k} p\mathrm{H} \qquad (54)$$

Or, if

$$\frac{b_o}{b_a + b_k} = \gamma_I$$

then

$$log\ j_c = const. - \gamma_I p\mathrm{H} \qquad (55)$$

When the discharge of hydrogen ions is the rate-determining process in hydrogen evolution, not only the reversible value of hydrogen potential but also the overpotential itself will be functions of pH (Chapter II). In this case:

$$log\ j_c = const. - \frac{b_k}{b_a + b_k} p\mathrm{H}; \qquad (56)$$

if

$$\frac{b_k}{b_a + b_k} = \gamma_{II}$$

$$log\ j_c = const. - \gamma_{II}\, p\mathrm{H} \qquad (57)$$

Normally, $b_k > b_o$ and the effect of pH will be more pronounced when the discharge of hydrogen ions is retarded. γ_I and γ_{II} may be calculated on the basis of polarization measurements and compared with the experimental value of γ (γ_{exp}). Results of this comparison[138] are given in Table 7.

For iron and nickel, a better agreement between the experimental and calculated values of γ is observed when the combination of adsorbed hydrogen atoms is assumed to be the slowest step in the process of hydrogen evolution. On the contrary, for zinc the calculated value of γ is nearer to the experimental one

TABLE 7 — COMPARISON OF γ_I AND γ_{II} WITH THE EXPERIMENTAL VALUE OF γ (γ_{exp}) FOR DIFFERENT METALS

Metal	b_k	b_a	γ_{exp}	γ_I	Deviation %	γ_{II}	Deviation %
Fe	0·125	0·075	0·26	0·30	16	0·62	134
Ni	0·100	0·076	0·30	0·34	13	0·57	90
Zn	0·13	0·03	0·97	0·38	61	0·82	15

when it is assumed that the discharge of hydrogen ions is the rate-determining stage.*

φ-Potential and the Distribution of Charges on the Surface of a Corroding metal. The value of the corrosion potential in the ϵ-scale is very important, as a knowledge of this value makes it possible to foresee the nature of the probable cathodic process, to estimate the rate of this process and so on. But, at the same time, on the basis of ϵ_c, it is quite impossible to make any suppositions regarding the charge of the corroding metal, the nature of particles being adsorbed on its surface, etc. An understanding of these and many other problems may be obtained[1,2] only when the null-point of the corroding metal is known and when the φ-scale of potentials is used.

Let us consider the corrosion of Cd and Zn in 0·1N HCl at room temperature. The corrosion potentials ϵ_c of Cd and Zn are equal to —0·51 V. and —0·75 V. respectively. Both these metals have negative values of ϵ_c, but their corrosion potentials in the φ-scale are very different. For Cd the corrosion potential is ${}_{Cd}\varphi_c = -0{\cdot}51 - (-0{\cdot}72) = 0{\cdot}21$ V. and for Zn, ${}_{Zn}\varphi_c = -0{\cdot}75 - (-0{\cdot}64) = -0{\cdot}11$ V. These values of φ_c indicate that during the course of corrosion of Cd its surface is charged positively with respect to the solution, and that considerable adsorption of anions is to be expected. In contrast, the surface of corroding zinc is charged slightly negatively and cations mainly will be adsorbed from the solution.

When the dissolution of a metal occurs as a result of the action of microgalvanic couples, it is normally assumed that

*In the case of zinc the simplifying assumptions made in deriving equation (53) are not very reliable, since the rate of discharge of zinc ions cannot be neglected. Equation (53) ought to be considered, therefore, only as a rough approximation.

cations are adsorbed on the inclusions of more noble metals acting as micro-cathodes, and on the surface of basic metals, the adsorption of anions is usually expected to take place. This conception is not always correct. The nature of particles being adsorbed on a certain metal depends not on the role they play in micro-galvanic cells, but on their values of φ-potential. There may exist all types of charge distribution along the surface of corroding commercial metals. Thus, if Cd has Ni as an inclusion, then on cathodic areas, the adsorption of cations will be observed while anions will be adsorbed on the anodic areas (Fig. 20). A second case, which is the reverse of the first one, may be expected when Cd-inclusions are present in zinc. Here anions will be adsorbed on the cathodes and cations on the anodes of the micro-galvanic cells (Fig. 21). The third case (inclusions of thallium in cadmium) is an example of anion adsorption on the whole

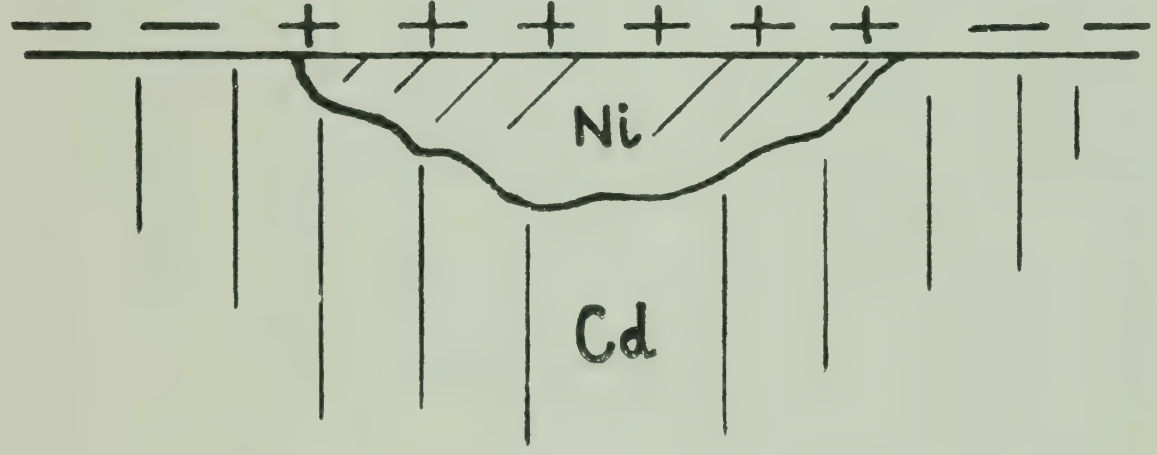

FIG. 20 — CHARGE DISTRIBUTION ALONG THE SURFACE OF CORRODING Cd WITH Ni INCLUSIONS (ACID SOLUTION) $_{Cd}\varphi_c > 0$, $_{Ni}\varphi_c < 0$

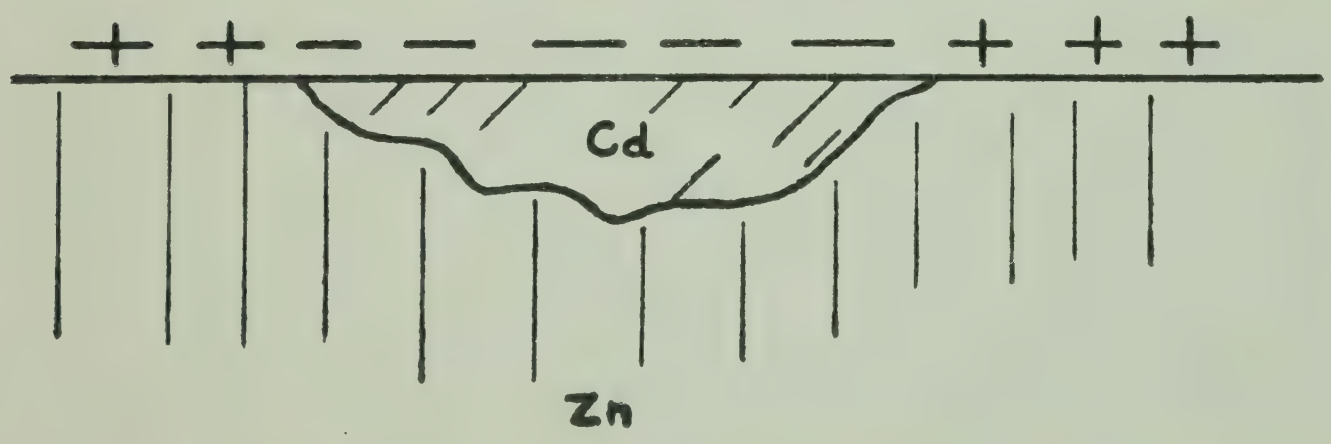

FIG. 21 — CHARGE DISTRIBUTION ALONG THE SURFACE OF CORRODING Zn WITH Cd-INCLUSIONS (ACID SOLUTION) $_{Zn}\varphi_c < 0$, $_{Cd}\varphi_c > 0$

surface of the corroding metals (Fig. 22). On all parts of the surface of zinc with iron inclusions the adsorption of cations alone takes place (Fig. 23).

From this point of view, the many deviations from the usual conception of charge distribution may be easily explained.

The φ-Potential of Corroding Metals and the Effect of Organic Corrosion Inhibitors. To protect iron and sevreal other metals from corrosion, organic compounds of different types are used. Their inhibition action is normally associated with the adsorption process which occurs on the metal-solution interface. The φ-scale of potentials gives a possibility of estimating the nature of the organic compounds to be adsorbed on the metallic surface under the given conditions. As it was shown above, the conditions of adsorption of the same compounds on the surface of different metals are similar if the values of φ-potentials of these metals are equal; that is

$$\varphi_1 = \varphi_2 = \varphi_3$$

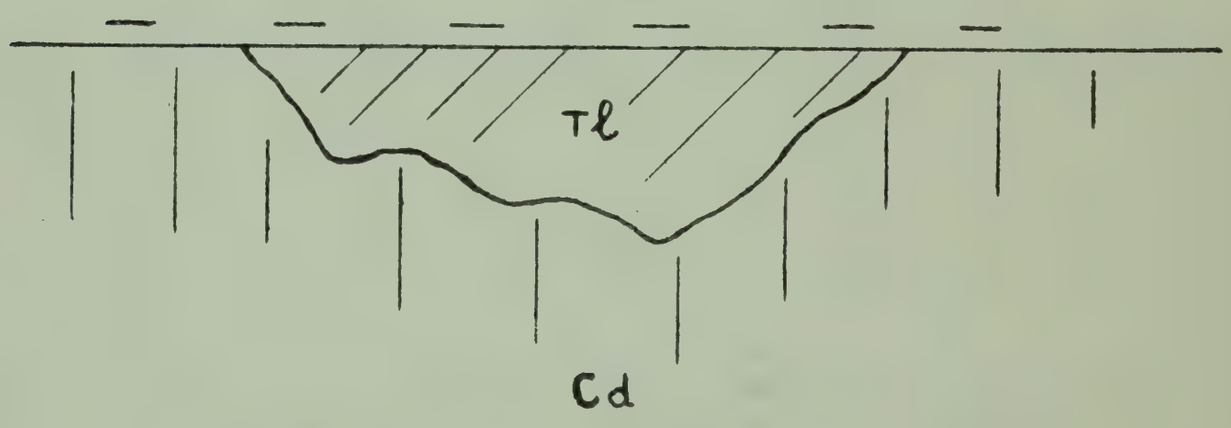

FIG. 22 — CHARGE DISTRIBUTION ALONG THE SURFACE OF CORRODING Cd WITH Tl-INCLUSIONS (ACID SOLUTION) ${}_{Cd}\varphi_c > 0$, ${}_{Tl}\varphi_c > 0$

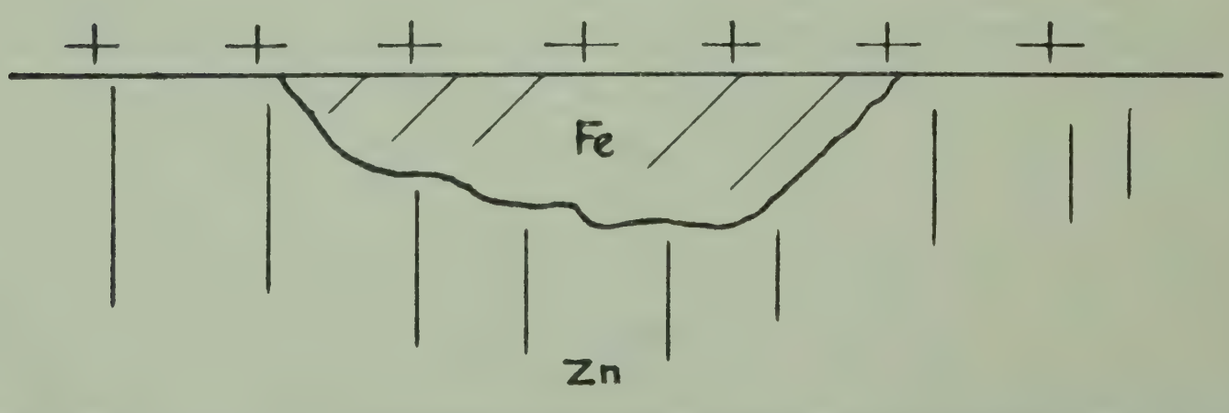

FIG. 23 — CHARGE DISTRIBUTION ALONG THE SURFACE OF CORRODING Zn WITH Fe-INCLUSIONS (ACID CORROSION) ${}_{Zn}\varphi_c < 0$, ${}_{Fe}\varphi_c < 0$

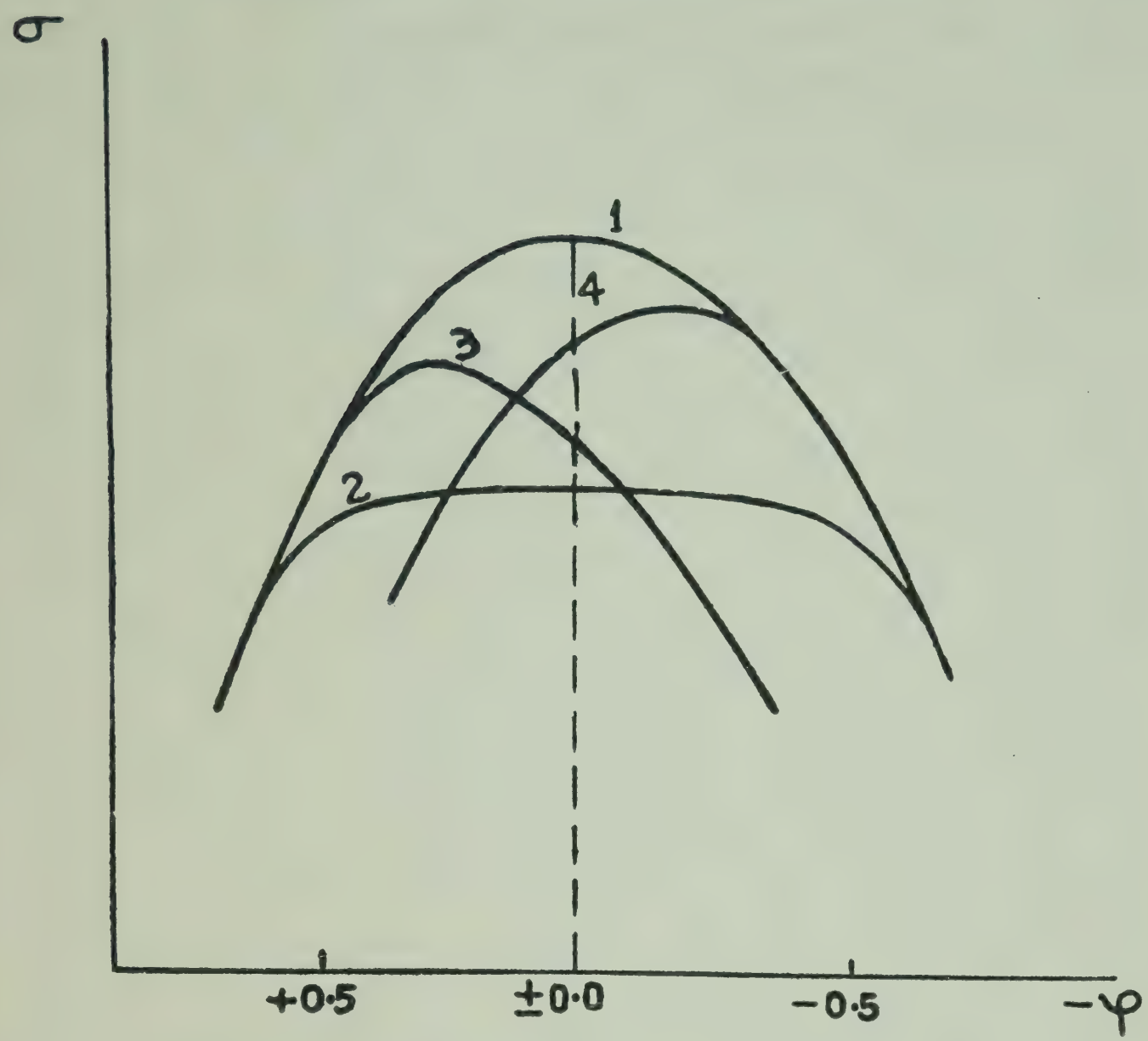

FIG. 24 — ELECTROCAPILLARY CURVES: (1) IN SOLUTION DEVOID OF ANY SURFACE ACTIVE COMPOUNDS; (2) IN PRESENCE OF MOLECULAR ORGANIC COMPOUND; (3) IN PRESENCE OF CATIONIC COMPOUND; AND (4) IN PRESENCE OF ANIONIC COMPOUND

Therefore, the data obtained for one of these metals may be used for all other metals, if the above condition (equality of φ-potentials) is obeyed.

Thus the electrocapillary curves obtained on mercury in the presence of certain organic compounds allow us to predict the adsorption of organic compounds on the surface of corroding metals*[2,3,125,139], for example, on the surface of corroding iron. Fig. 24 represents four electrocapillary curves which correspond to pure solution of sulphuric acid and to the same solution but with non-ionic, cationic and anionic organic compounds added respectively. The values of potential are given here in the

*A similar approach was adopted several years later by De, C. P., *Nature, Lond.*, **180** (1957), 803.

φ-scale. The corrosion of iron in sulphuric acid occurs at the potential ϵ_c approximately equal to $-0{\cdot}28$ V. and since ${}_{Fe}\epsilon_{q=0} = -0{\cdot}02$, the corrosion potential of iron given in the φ-scale will be equal to ${}_{Fe}\varphi_c = -0{\cdot}28 - (-0{\cdot}02) = -0{\cdot}26$ V. At this value of potential, the adsorption of the chosen anionic organic compound does not take place, and it cannot perform any inhibitory action. Both molecular and cationic organic compounds may be adsorbed under the given value of φ-potential and their inhibition effect may, therefore, be expected. If the inhibition efficiency is determined mainly by adsorption, then the cationic organic compound ought to be the best inhibitor here. This conclusion is in good agreement with the well-known fact that the dissolution of iron in acid media may be successfully diminished or even eliminated by amines as well as by many other cationic organic compounds.

If the conditions of the corrosion process are changed, for example, the dissolution of iron occurs not in pure sulphuric acid, but in sulphuric acid containing some oxidizing agent (e.g. ferric salt), the effect of inhibitors will also be altered due to the change in the corrosion potential. In the presence of an oxidizing agent, the corrosion potential will be shifted to more positive values. Let the new value of φ_c be equal to $+0{\cdot}3$ V. Under these conditions, the cationic organic compounds will be ousted from the surface of the metal, their surface concentration becomes negligibly small and a decrease in the rate of corrosion due to their presence in solution cannot be expected. On the contrary, anionic organic compounds will be highly adsorbed on the metal-solution interface and will act as effective inhibitors. Molecular organic compounds would still remain adsorbed on the surface of metal and may prevent corrosion.

These conclusions are in good agreement with the observations made by Elze and Fischer*[140,141], who found that cationic inhibitors — though very effective in pure acid solutions — lose their activity when the corrosion of iron takes place in oxidizing media.

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*The explanation given by Elze and Fischer is based on the assumption that inhibitors only influence the reaction $2H \longrightarrow H_2$. In the presence of an oxidizing agent, since the nature of the cathodic process is changed, no inhibitor action will be observed. These authors, however, did not take into account the alteration of the corrosion potential, and consequently the change in the conditions of adsorption. Moreover, the change in the efficiency of an inhibitor may also be due to the fact that the electrode process becomes diffusion-controlled.

The same consideration may be applied to any other metal if its corrosion potential in the φ-scale is known.

On the basis of the φ-scale of potentials, it is possible not only to limit the number of probable inhibitors and hence to make the search for suitable compounds easier, but also to give a more complete picture of the nature of the action of inhibitors.

Before discussing some aspects of the action of inhibitors, a point which pertains to corrosion diagrams will now be emphasized. It has been mentioned earlier that there is a sudden change of hydrogen overpotential in the region of potentials around the null point of a metal belonging to the Electrochemical Group II. Care should, therefore, be taken in estimating the rate of corrosion on the basis of polarization experiments. It is important that experiments should not be carried out only on a negatively charged surface of a corroding metal, and the results then extrapolated. By doing so, we ignore the fact that when the corrosion potential of a metal of Electrochemical Group II is more

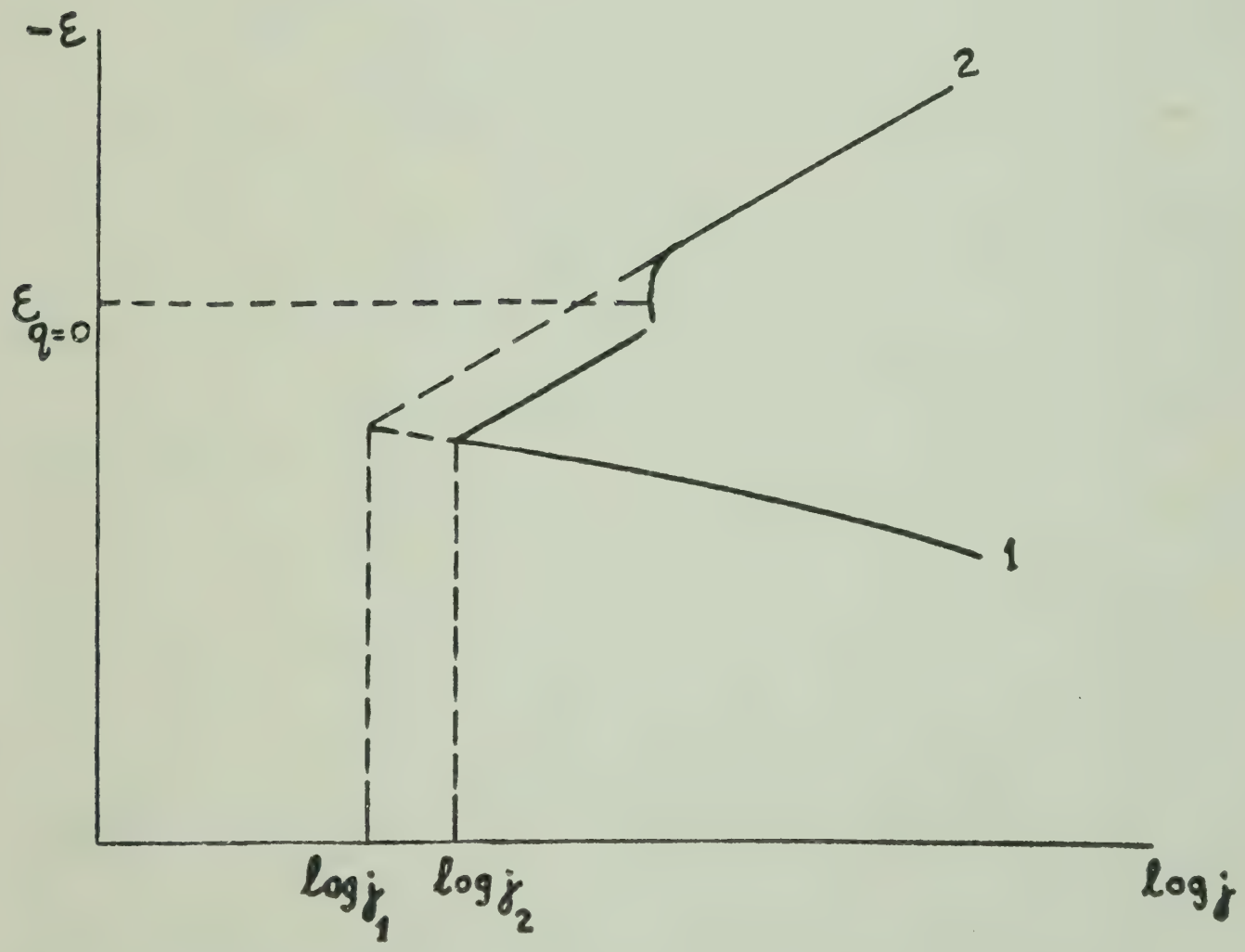

FIG. 25 — DIAGRAM SHOWING THE EFFECT OF A CHANGE IN THE SIGN OF THE CHARGE ON THE METAL SURFACE ON THE CORROSION RATE AND ON THE CORROSION POTENTIAL

positive than its null point, there is a sudden drop in polarization at the null point (Fig. 25), which results in a greater rate of corrosion (j_2) than would be expected (j_2)[142].

Let us now consider the above corrosion system, but in this case altered by the addition of an organic inhibitor. The shape of the normal cathodic polarization curve (Fig. 26, curve 2) is changed to curve 3. It will be noticed that the increase of cathodic potential when the metal surface is negatively charged with respect to the solution (i.e. $-\epsilon > \epsilon_{q=0}$) is much less than the increase when the surface is positively charged (i.e. $-\epsilon < \epsilon_{q=0}$).

This phenomenon can be explained on the following lines. In general, the action of an inhibitor arises not only from an adsorption of the inhibitor molecules on the metal surface, but also

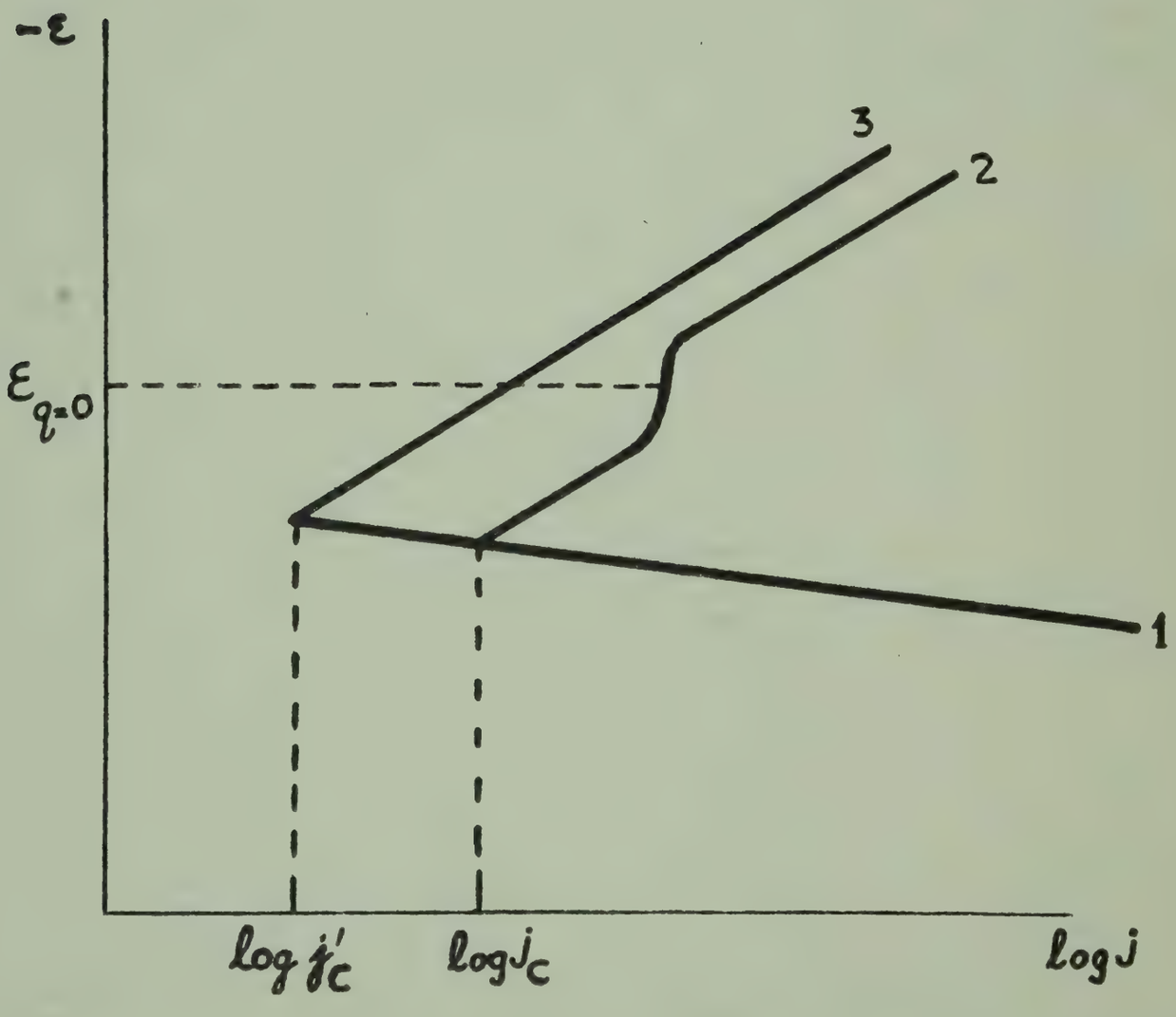

FIG. 26 — THE EFFECT OF A MOLECULAR ORGANIC COMPOUND ON THE CATHODIC POLARIZATION CURVE, THE CORROSION POTENTIAL AND THE RATE OF CORROSION. (1) THE ANODIC POLARIZATION CURVE; (2) CATHODIC POLARIZATION CURVE IN AN ACID SOLUTION; (3) THE SAME AS 2, BUT IN PRESENCE OF AN ORGANIC INHIBITOR

from a partial desorption of those particles which are normally adsorbed in the absence of the inhibitor. On a positively charged metal, it will be the anions that are partially displaced by the inhibitor. The anions, however, lower the activation energy for the discharge of hydrogen ions (*see* Chapter III). By displacing the anions, the inhibitor increases the activation energy, and thus increases the hydrogen overpotential. Therefore, this effect on the overpotential adds to the effect of the inhibitor itself.

It should be mentioned again that experiments performed only on a negatively charged metal surface would give for the decrease of the corrosion rate due to the presence of the inhibitor values which are much less than is actually the case.

The adsorption of an organic compound may also affect the adsorption of hydrogen. As far as the combination of hydrogen atoms is concerned, adsorption of the inhibitor molecules can affect the situation in two opposite ways. On the one hand, the heat of hydrogen adsorption is lowered and, therefore, combination of hydrogen atoms is facilitated*; and on the other hand, the rate of combination of hydrogen atoms is cut down due to the spatial hindrance caused by the adsorbed inhibitor particles. The final effect, however, will depend on the relative magnitude of these two effects.

We shall now consider the effect of the adsorption of inhibitor on the discharge of hydrogen ions. In the case of metal corrosion in acid solutions the solution side of the electrical double layer consists of hydrogen ions mainly. The decrease of the heat of hydrogen adsorption in the presence of organic compounds will increase the energy of activation for the discharge of hydrogen ions. Moreover, the adsorbed particles of the organic compound will replace some of the hydrogen ions, reducing their surface concentration and making their discharge more difficult. This poisoning effect of organic compounds on the discharge of hydrogen ions would be more pronounced in the case of surface active organic cations or cationic-type complexes, since the hindering influence of the electric field will also affect the situation. Therefore, the influence of various organic compounds on the

---

*Kobozev and Nekrasov[18] have drawn the attention of electrochemists to the important role of heat of adsorption of hydrogen in cathodic evolution.

two main stages of the hydrogen evolution reaction may not be the same, and a change of mechanism of this reaction may be expected as a result the addition of inhibitors.

This may be illustrated by Fig. 27, where the relationship between the rate of corrosion of iron and the *p*H of solution is shown[143]. In the absence of organic compounds, experiment shows that the slope of the $log\ j_c - pH$ curve is very near the value of γ_I, corresponding to the slow combination of hydrogen atoms. After adding a cationic inhibitor (tetrabutylammonium sulphate) the slope of the $log\ j_c - pH$ curve is changed, and the new value of γ_{exp} is in a good agreement with γ_{II} calculated on the basis of the theory of retarded discharge of hydrogen ions. The increase of hydrogen overpotential is, therefore, not necessarily connected with the increase of surface concentration of hydrogen atoms. In many cases, especially when cationic inhibitors of corrosion are used, the amount of adsorbed hydrogen atoms is decreased. This is important when one wants to avoid the

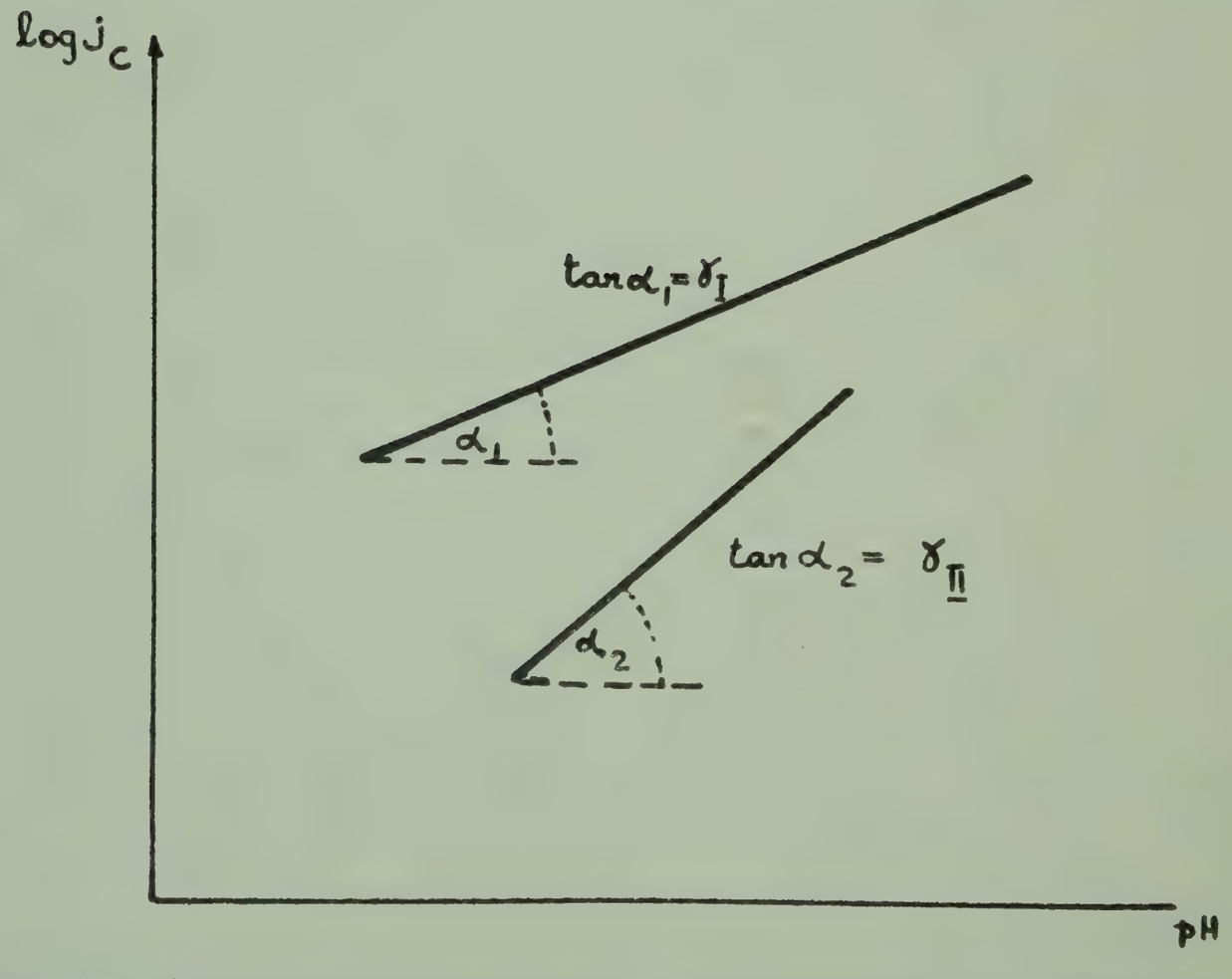

FIG. 27 — THE CHANGE OF THE SLOPE OF THE CORROSION RATE — *p*H CURVE DUE TO THE PRESENCE OF A CATIONIC ORGANIC COMPOUND

diffusion of hydrogen into the body of the metal. In this sense the addition of cations to pickling baths is most preferable.

It is evident that on the basis of the φ-scale of potentials, the selection of organic corrosion inhibitors may be made easier. For practical purposes, it is necessary, however, to know not only the nature of the organic compound, but also its optimum concentration.

Here, again, the φ-scale may be used[139,144,145]. The natural assumption is that the inhibition activity of a non-reducible organic compound will increase regularly with its surface concentration. The change of surface concentration with volume concentration may be estimated with the help of electrocapillary curves, electrical capacity measurements and many other methods. Normally all these measurements are carried out on mercury and only the results obtained at a φ-potential equal to the corrosion potential of the metal should be taken into account.* The electrocapillary curves given in Fig. 28 correspond to different amounts of 2,6-dimethylquinoline added to 1N H_2SO_4. The corrosion potential of iron varies slightly with the amount of 2,6-dimethylquinoline but, as a first approximation, a constant value of φ_c equal to $-0{\cdot}26$ V., was taken. The relation between $\Delta\sigma$ (the decrease in interfacial tension due to the addition of an organic compound) and the logarithm of its volume concentration ($log\ C$) is approximately linear. A linear relationship is also found in many cases when some other organic compounds are present. Thus

$$log\ \Delta\sigma = const._{\sigma} + \beta_{\sigma}\ log\ C \qquad (58)$$

This equation can be derived from Gibbs' adsorption equation making certain assumptions:

(i) The relation between surface concentration C' and volume concentration C is represented by Freundlich's isotherm or by a similar type of isotherm as follows:

$$C' = K_f C^{\beta}$$

(ii) The excess of surface concentration Γ is considered as equal to the surface concentration itself:

$$\Gamma = C',$$

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*Suppression of polarographic maxima may also be utilized for this purpose[146,147]. The difficulty is that the position of maxima usually does not correspond to the corrosion potential.

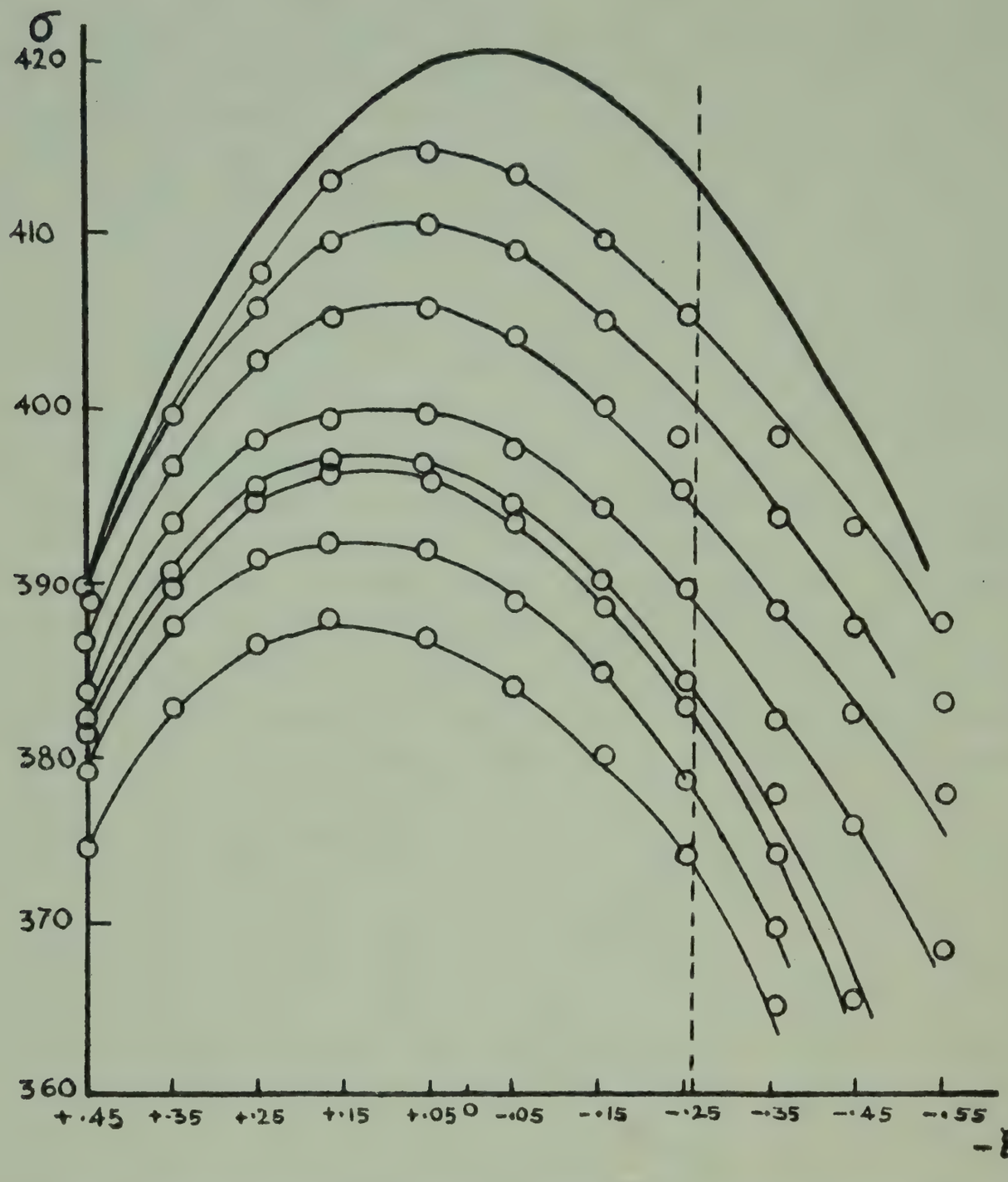

FIG. 28 — ELECTROCAPILLARY CURVES OBTAINED ON MERCURY IN 1N H_2SO_4 (THICK LINE) AND IN PRESENCE OF DIFFERENT AMOUNTS OF 2,6-DIMETHYL-QUINOLINE (INCREASING CONCENTRATION IN DOWNWARD ORDER)

(iii) The variation of corrosion potential with the volume concentration of the organic compound is neglected ($\epsilon_1 = \epsilon_2 = \epsilon_c$).

$$\epsilon_c = const.$$

Then, from Gibbs' formula

$$\Gamma = -\frac{d\sigma}{d\mu} = -\frac{d\sigma}{RTdlnC} \qquad (59)$$

or,

$$C' = -\frac{d\sigma}{RTdlnC},$$

$$-d\sigma = RT\frac{C'dC}{C},$$

and

$$-d\sigma = RT\frac{K_f C^{\beta}}{C}dC = RTK_f C^{(\beta-1)}dC \qquad (60)$$

After integration,

$$-\sigma = \frac{RT}{\beta}K_f C^{\beta} + const.,$$

since at $C = 0$, σ ought to be equal to σ_o, the integration constant is equal to $-\sigma_o$, and

$$\sigma_o - \sigma = \Delta\sigma = \frac{RT}{\beta}K_f C^{\beta} \qquad (61)$$

Or,

$$log\ \Delta\sigma = log\frac{RT}{\beta}K_f + \beta\ log\ C \qquad (62)$$

which is identical to the empirical equation (58).

It was assumed that for the given organic compound its inhibition action increases regularly with the surface concentration. On this basis, an expression correlating the inhibition coefficient K_i* with the volume concentration of the inhibitor can be obtained.

The energy of activation of the rate-determining stage of the corrosion process will increase in the presence of adsorbed inhibitor particles and it can be represented as a linear function of the logarithm of the surface concentration. Thus,

$$U_i = U^o + RTlnC'\delta$$

where δ is a factor which takes into account some specific properties of organic inhibitors (dimensions for example). Then the rate of corrosion in the presence of inhibitor will be given as

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*The inhibition coefficient is defined as the ratio of the rate of corrosion in the absence of inhibitor (j) to that in the presence of definite amount of inhibitor (j_i), i.e. $K_i = \frac{j}{j_i}$.

$$j_i = K \ exp \left(- \frac{\alpha_2 \epsilon_2 F - RT ln C' \delta}{RT} \right)$$

In accordance with the above assumptions, $\epsilon_1 = \epsilon_2 = \epsilon_c$, $\alpha_1 = \alpha_2$ and

$$K_i = \frac{j}{j_i} = C' \delta \tag{63}$$

If Freundlich's isotherm is true,

$$K_i = {}_{Fe}K_f C^{\beta} \delta,$$

or,

$$log \ K_i = log_{Fe} \ K_f \delta + \beta \ log \ C \tag{64}$$

$$log \ K_i = const._k + \beta_k \ log \ C \tag{65}$$

This equation was verified for many organic compounds and was found to be in fairly good agreement with the experimental corrosion data[144,145].

The slope β in equations (58) and (65) has the same value when the change of surface tension of mercury with the concentration of the given organic compound is measured at a φ-potential corresponding to the corrosion potential of iron given in the φ-scale. This justifies the assumption that adsorption conditions are similar on different metals provided their φ-potentials are equal.

It is obvious that the coincidence of the values of β in equations (58) and (65) makes it possible to estimate the concentration of the inhibitor at which the rate of corrosion will be decreased up to a desired level by using only one value of inhibition coefficient K_i and from electrocapillary measurements on mercury. In this case, it is not necessary to carry out direct corrosion experiments which take considerable time. Moreover, the same electrocapillary curves may be used when the conditions of corrosion are changed, by taking into account the new values of φ-potentials.

The experimental data which have been obtained so far confirm these ideas in general, but at the same time the data indicate that surface activity is not the only factor which determines the inhibition properties of organic compounds. Two organic compounds with equal surface activities but having different functional groups may display different inhibition efficiencies. Hence, the nature of the functional group present in an organic molecule is also of great importance. This is probably because the contribution of a functional group to the surface activity of an

organic compound need not be the same as its contribution to the efficiency of inhibition. Thus, for example, thiourea is a much more efficient corrosion inhibitor than β-naphthoquinoline though the surface activity of these two compounds (measured under comparable conditions) is almost the same. It may be concluded, therefore, that the surface activity is the predominating factor only within a given class of organic compounds having the same functional group.

In order to prove this conclusion the experimental data describing the effect of various nitrogen-containing inhibitors on the rate of acid corrosion of iron has been correlated with the surface activity of the same compounds as measured on a mercury electrode. The comparison has been made at the value of φ-potential which corresponds to the corrosion potential of iron ($_{Fe}\alpha_c = -0{\cdot}26$ V.). Small deviations from the mean value of ϵ_c due to the addition of inhibitors have been neglected. The list of compounds along with the values of $\beta\sigma$ and const.$_\sigma$ of equation (58) is presented in Table 8.

TABLE 8 — β_σ AND CONST.$_\sigma$ VALUES FOR DIFFERENT NITROGEN-CONTAINING ORGANIC COMPOUNDS

Organic compound	β_σ	Const.$_\sigma$
1. Piperazine	0·22	1·03
2. Diethylamine*	0·41	1·15
3. Pyridine*	0·37	1·34
4. Aniline*	0·64	1·46
5. Quinoline*	0·29	1·76
6. Di-*n*-butylamine	0·30	1·77
7. Di-methylaniline	0·40	1·79
8. Ethylaniline	0·36	1·83
9. Anthranilic acid†	0·43	1·94
10. Caffeine†	0·32	1·97
11. 2-methylquinoline	0·29	1·99
12. Diethylaniline	0·42	2·02
13. Pyramidone†	0·39	2·08
14. O-oxyquinoline†	0·39	2·16
15. 2,6-dimethylquinoline	0·31	2·19
16. Brucine	0·23	2·29
17. β-naphthoquinoline†	0·29	2·34

*Antropov, L. I. & Banerjee, S. N., *J. Indian chem. Soc.*, **35** (1958), 531.

†These values have been obtained by Antropov, L. I. *et al.*, *Proc. Novotscherkassk Polytech. Inst.*, **69/83** (1958), 129. The other results are from a paper by Antropov, L. I. & Banerjee, S. N. which is in the course of publication.

Fig. 29 represents the functional relationship which exists between $const._k$ and $const._\sigma$. Though the values of $const._k$ have been calculated from data obtained by different authors[148-150], all the points are situated near the same common straight line; the disparity between the values obtained under similar conditions by different authors is in general greater than the scattering of experimental points around the straight line which can be represented by a simple equation.

$$const._k = -0{\cdot}8 + const._\sigma \qquad (66)$$

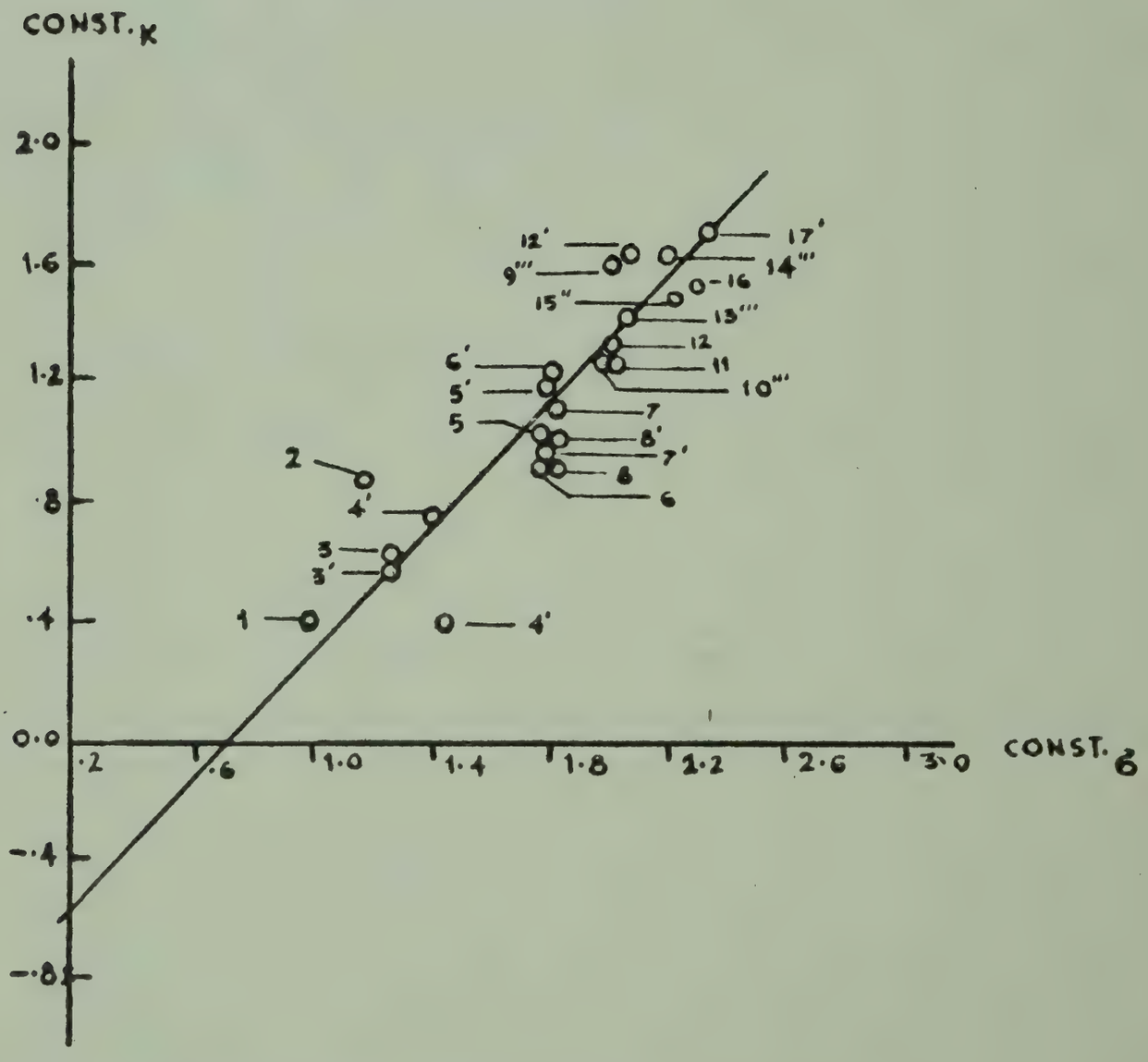

FIG. 29 — RELATIONSHIP BETWEEN CONST.$_k$ AND CONST.$_\sigma$ OF EQUATIONS (58) AND (65) RESPECTIVELY. THE POINTS ARE NUMBERED TO INDICATE THE COMPOUNDS AS THEY ARE NUMBERED IN TABLE 8. THE SUPERSCRIPT ′ INDICATES THAT THE CORROSION DATA OF MANN ARE USED, ″ THAT OF HOAR AND HALLIDAY AND ‴, THE CORROSION AND ELECTROCAPILLARY DATA OF ANTROPOV *et al.* NUMBERS WITHOUT SUPERSCRIPT CORRESPOND TO RIDE'S DATA

TABLE 9 — EXPERIMENTAL AND CALCULATED VALUES OF K_i FOR DIFFERENT CONCENTRATIONS OF di-*n*-BUTYLAMINE

CONCENTRATION *mole/l.*	K_i (EXPERIMENTAL)	K_i (CALCULATED)
$3{\cdot}6\times10^{-3}$	1·7	1·7
$7{\cdot}1\times10^{-3}$	1·9	2·0
$2{\cdot}1\times10^{-2}$	2·5	2·8
$3{\cdot}6\times10^{-2}$	3·1	3·5
$7{\cdot}1\times10^{-2}$	4·8	4·2
$1{\cdot}8\times10^{-1}$	7·7	5·7

This parallelism between inhibition efficiency and surface activity, and also the coincidence of the values β_σ and β_k observed at the same value of φ-potential suggests the possibility of calculating only on the basis of electrocapillary measurements the inhibition coefficients for any nitrogen-containing compounds included or not included in Table 8. To make this calculation the following equation (67) should be used:

$$\log K_i = -0{\cdot}8 + const._\sigma + \beta \log C \qquad (67)$$

Unfortunately there does not appear to be any data both for surface activity and inhibition efficiency at various concentrations of organic compounds. To illustrate the applicability of equation (67), the calculated and experimental[148] values of K_i for di-*n*-butylamine are collected in Table 9.

It can be seen that in some cases the agreement between the observed and calculated values is better and in other cases worse. Nevertheless the agreement is as good as the agreement between the experimental data obtained by different authors[148-150]. The calculation of the rate of corrosion in presence of different amounts of the inhibitor needs only the knowledge of the rate of corrosion in acid solutions not containing any additives. It is appropriate to stress once again that while the surface activity of organic compounds is measured on mercury, the inhibition efficiency is studied on iron. The correlation of these two series of results is only possible when the φ-scale of potentials is used.

Work is now in progress to study the relationship between the surface activity and the inhibition efficiency of organic compounds having different functional groups.

Protection by Means of Organic Inhibitors and by Cathodic Polarization. Protection by means of cathodic polarization from an external source of e.m.f., or by introducing a "sacrificial" anode in the corrosion environment may be better understood on the basis of a full corrosion diagram (Fig. 30). This diagram is simplified in the sense that real polarization curves are represented by straight lines. Normally, this is not the case, but for the present purpose this simplification may be adopted.

The intersection of anodic and cathodic polarization curves corresponds to the corrosion potential ϵ_c and to a rate of corro-

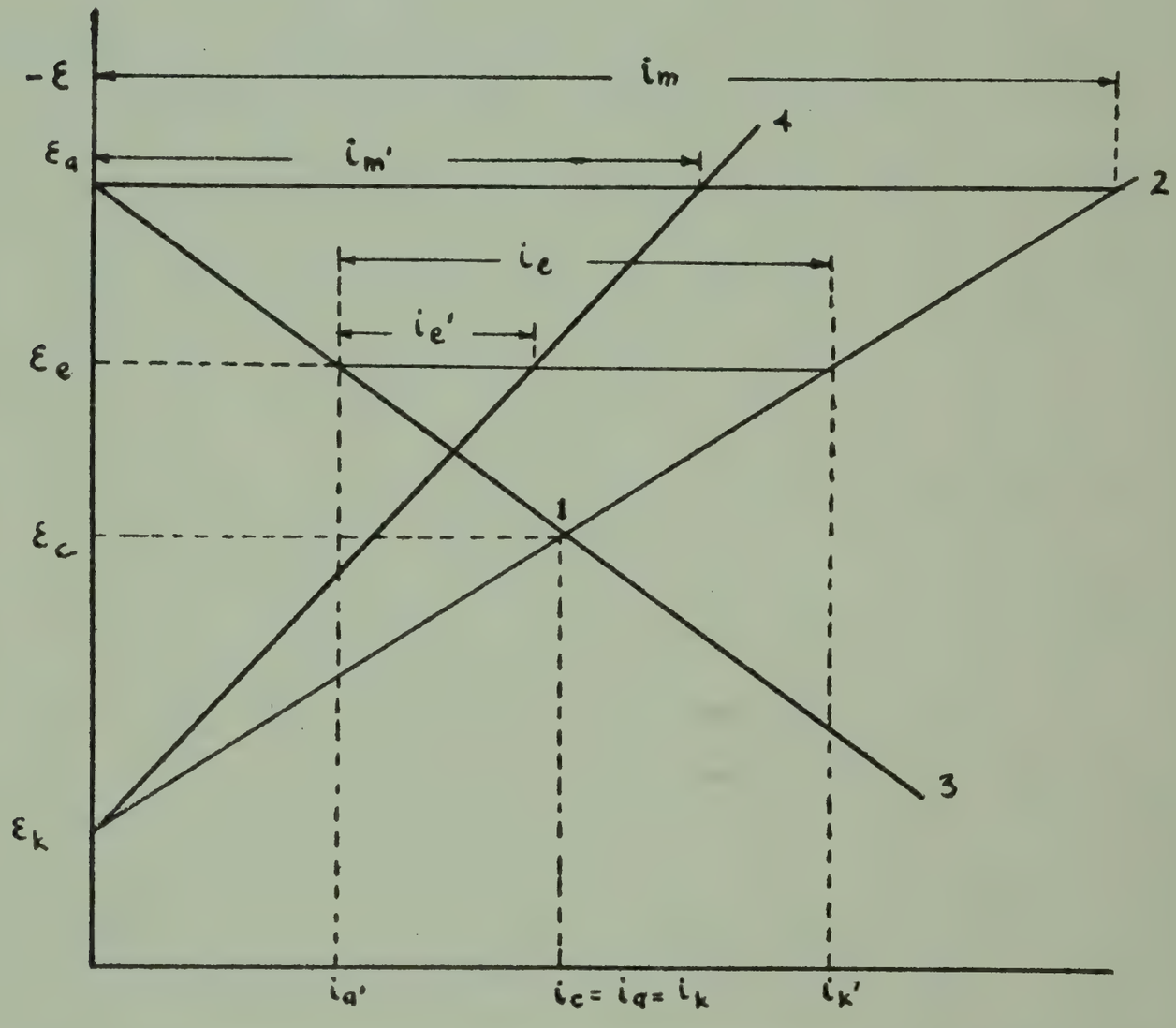

FIG. 30 — CORROSION DIAGRAM SHOWING THE PRINCIPLES OF CATHODIC PROTECTION IN AN ACID MEDIUM WITHOUT AND IN THE PRESENCE OF AN ORGANIC INHIBITOR. THE SYMBOLS i_a AND i_k DENOTE THE RATES OF ANODIC AND CATHODIC PROCESSES (GIVEN IN UNITS OF CURRENT) WHICH CORRESPOND TO A STEADY STATE PROCESS OF CORROSION, i_a' AND i_k' CORRESPOND TO A PROCESS OF CORROSION UNDER EXTERNAL APPLIED CURRENT. i_e AND i_e' ARE THE VALUES OF EXTERNAL CURRENT LEADING TO A DEFINITE RATE OF CORROSION (i_a') WITHOUT AND IN PRESENCE OF INHIBITOR RESPECTIVELY. i_m AND i_m' CORRESPOND TO THE EXTERNAL CURRENT RESULTING IN A COMPLETE PROTECTION OF A METAL WITHOUT AND IN PRESENCE OF AN INHIBITOR RESPECTIVELY

sion i_c. The straight lines to the right of the intersection can only be obtained by cathodic polarization (1-2) or by anodic polarization (1-3) respectively. Cathodic polarization will shift the stationary potential to more negative values. At the intersection, the anodic current i_a is equal to cathodic current i_k and both of them are equal to the rate of corrosion i_c, i.e.

$$i_a = i_k = i_c$$

When there is impressed a certain cathodic current i_e, then its value will be equal to the difference between the cathodic and anodic currents ($i_{k'}$ and $i_{a'}$ respectively) at a new value of potential ϵ_c (Fig. 30). When the potential of the corroding metal is equal to the initial anodic potential ϵ_a, the current required will be equal to i_m. Normally, the impressed cathodic current which provides for the desired protection is high and the consumption of electricity or sacrificial anodes is also high; this method of protection is, therefore, rather wasteful.

This disadvantage may be, to some extent, overcome if cathodic polarization is combined with the addition of organic inhibitors to the metal surroundings[3,125,151]. The nature of inhibitors which would be effective in this case depends on the position of the null point of the corroding metal with respect to the corrosion potential, i.e. it depends on the value of φ_c. Let the corrosion of iron in sulphuric acid be taken as an illustrative example. In this case ${}_{Fe}\varphi_c = -0{\cdot}26$ V. and for ϵ_a, it is possible to give only a very approximate value which is about $-0{\cdot}6$ V. This means that the intersection (1) is more negative than the null point of the metal. The initial anodic potential ϵ_a is very remote from the null point of iron. It is evident (Fig. 24) that by applying the external cathodic current, only the adsorbility of cations on the surface of iron will be increased. The surface concentration of both anionic and molecular organic compounds under these conditions will be less than at ϵ_c. The increased amount of adsorbed cationic organic compounds will affect the course of both the cathodic and the anodic processes. As a first approximation, it can be assumed that only the cathodic polarization curve† will be subject to alteration according to Fig. 30 and the

*The current density required for complete protection is the function of cathodic polarization only and does not depend on the value of anodic polarization.

current density required for partial or for complete (curve $\epsilon_k - 4$) protection of iron will be very much decreased. The effect of this combined method of protection is normally greater than the sum of single effects arising as the result of inhibitor action or cathodic protection separately.*

The same method of consideration may be applied to any other case of corrosion. Thus, for example, if cadmium is chosen instead of iron, it may be shown that in this case cathodic protection will give the best effect when combined with certain non-ionic organic compounds. The ϵ_a-value of Cd in acid solution is more positive than ${}_{Cd}\epsilon_{q=0}$ and adsorption of cations cannot be normally attained.

It is well known that many of the organic inhibitors of corrosion of iron in acids including those of cationic nature are not effective in neutral media, for example in sea water. At the first sight, this seems to contradict the theory developed above as the corrosion potential of iron in neutral solution is more negative (normally −0·5 V.) than in acid solution and the conditions are more favourable for adsorption of cations. But, it is necessary to take into account the different mechanism of corrosion of iron in neutral solution as compared with acid solution. The rate of corrosion of iron is usually determined by the transport of oxygen which plays here the role of depolarizing agent. The corrosion diagram which corresponds to iron corrosion in neutral media is shown in Fig. 31. If the organic compound changes the anodic and/or the cathodic polarization, it will not affect the rate of corrosion and the value of i_c will remain the same (Fig. 31). But the influence of organic compounds will be quite pronounced when the external current is applied and a considerable decrease of current density required for obtaining the same degree of suppression of corrosion would be expected in the presence of an organic compound. Therefore, the combined method of corrosion protection can also be used in neutral media†.

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*A more detailed consideration of the simultaneous effect of cathodic polarization and addition of inhibitors can be found in the paper of Antropov, L. I., *J. sci. industr. Res.*, **18B** (1959), 314.

†Increase of protection efficiency when inorganic inhibitors are used in combination with cathodic polarization is not due to the adsorption phenomena described above, but mainly due to the liquid near the corroding sample being rendered alkaline[152,153].

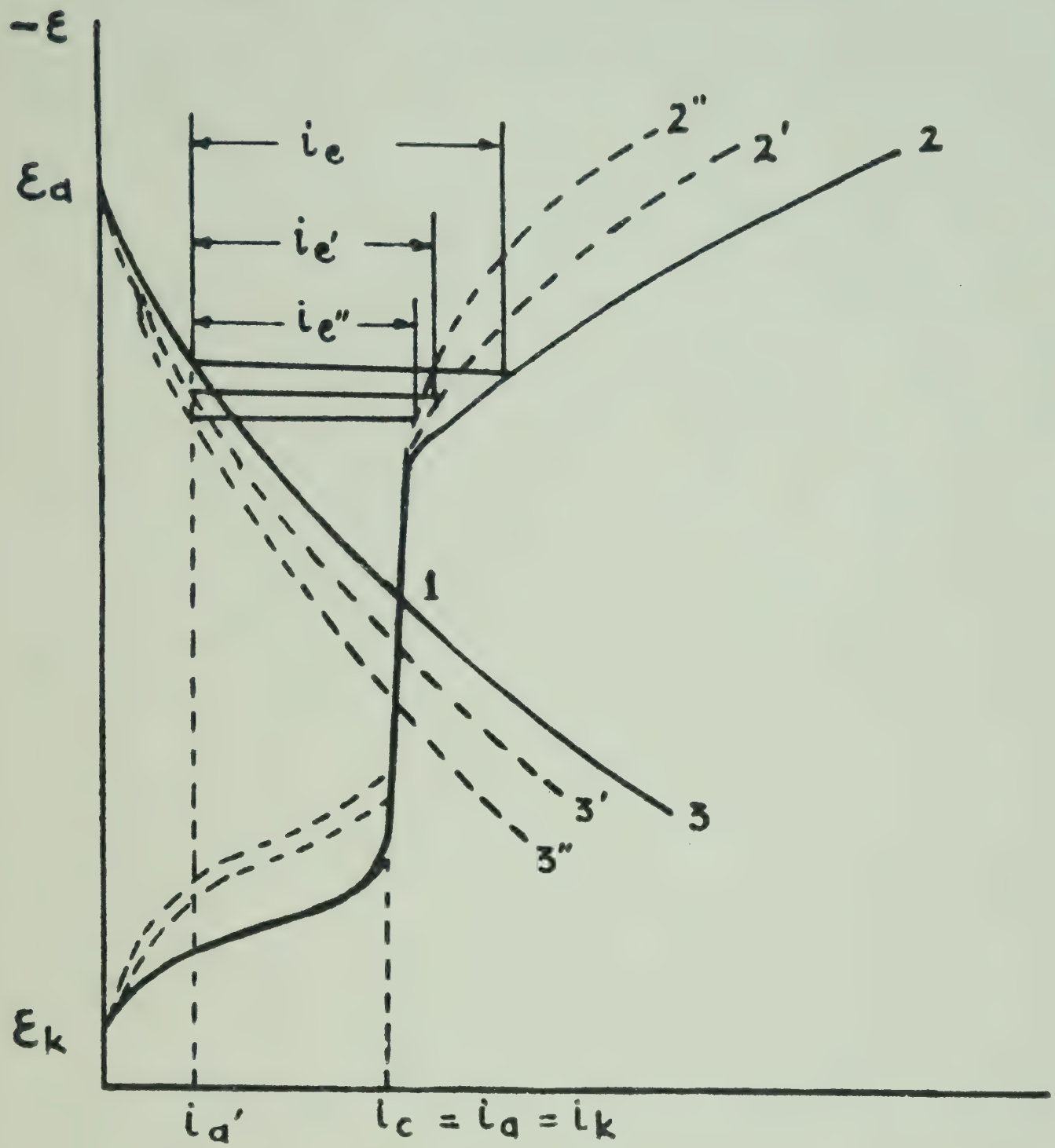

FIG. 31 — DIAGRAM REPRESENTING IRON CORROSION IN NEUTRAL MEDIUM AND THE EFFECT OF INHIBITORS COMBINED WITH CATHODIC POLARIZATION. CURVES $\epsilon_a - 3$ AND $\epsilon_k - 2$ CORRESPOND TO POLARIZATION CURVES OBTAINED IN A NEUTRAL SOLUTION WHICH DOES NOT CONTAIN ANY ADDITIONS. CURVES $\epsilon_a - 3'$, $\epsilon_a - 3''$ AND $\epsilon_k - 2'$, $\epsilon_k - 2''$ CORRESPOND TO POLARIZATION CURVES OBTAINED IN PRESENCE OF TWO DIFFERENT INHIBITORS. i_e, i_e' AND i_e'' CORRESPOND TO THE VALUES OF EXTERNAL CURRENT WHICH SHOULD BE APPLIED TO OBTAIN THE SAME RATE OF CORROSION i_a'

A Special Type of Corrosion — Simultaneous Deposition of Noble Metal on the Surface of a Baser Metal. If a sample of iron or mild steel is immersed in a solution containing copper sulphate and sulphuric acid, the process of exchange between Cu-ions and metallic iron will start immediately. As a result of this process, a coarse and incoherent deposit of copper

is formed. Since the deposit is porous, the dissolution of iron and discharge of copper ions will proceed, though at a lower rate than the rate at the initial stage of contact exchange. The appearance of a contact copper deposit prevents us from utilizing the simple sulphate electrolytes for copper plating on iron or on mild steel.

Contact deposition of copper on iron may be considered as a special case of a purely heterogeneous electrochemical corrosion with certain typical features: (i) copper ions act here as a depolarizer, (ii) the ratio of cathodic to anodic areas varies during the course of corrosion from 0 to 1 (approximately), and (iii) the corrosion potentials range from the value roughly equal to the stationary potential of iron in acid solution to the stationary potential of copper in the solution of copper sulphate. The simplified corrosion diagram for the $Fe - Cu - CuSO_4 - H_2SO_4$ system is given in Fig. 32. The i_{max} represents the maximum

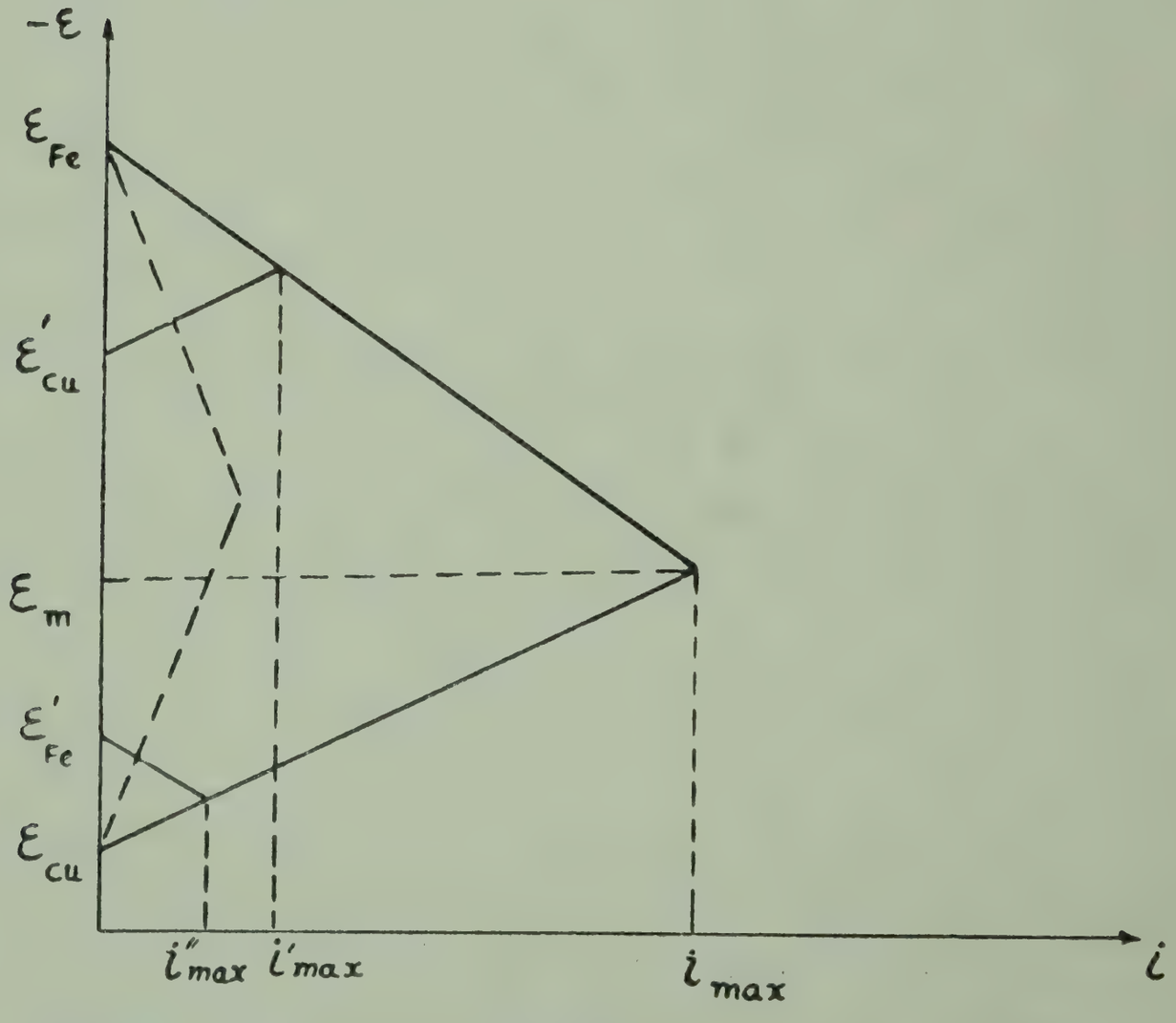

FIG. 32 — DIAGRAM OF THE PROCESS OF CONTACT EXCHANGE BETWEEN METALLIC IRON AND COPPER IONS IN SOLUTION

rate of corrosion which corresponds to the potential ϵ_m. The suppression of contact exchange is normally attained in two ways:

(1) The initial potential of the cathodic process (ϵ_{Cu}) is shifted to more negative values. For example, in pyrophosphate electrolytes the position of the initial cathodic potential corresponds to ϵ'_{Cu} and the rate of exchange (i'_{max}) is considerably reduced. In electroplating practice, the cyanide complex baths are used where the copper-potential is more negative than the iron-potential and the process of contact exchange is completely eliminated.

(2) The initial potential of the anodic process (ϵ_{Fe}) is shifted to more positive values. In electroplating practice, the iron articles are plated by nickel before galvanizing them in a copper-sulphate bath. The potential of normally passivated nickel (ϵ'_{Fe}) is very near to the potential of copper.

It follows from the corrosion diagram that besides these two well-known methods, the same results may be obtained if both the cathodic and anodic polarizations are highly increased (dotted lines in Fig. 32). In this case, initial potentials do not undergo any visible change, but the rate of the exchange process is reduced due to the decrease of the rate of the particular cathodic and anodic reactions as a result of inhibitors added to the sulphate electrolyte[154]. The selection of proper inhibitors may be done on the basis of the φ-scale of potentials provided the change of potential during the course of contact exchange and the values of copper and iron null points are known. A typical curve which represents the potential-time relationship during the contact exchange between metallic iron and copper solutions is given in Fig. 33.

The initial value of potential is between $-0{\cdot}15$ and $-0{\cdot}20$ V., which is more negative than the null points of iron ($_{Fe}\epsilon_{q=0} = -0{\cdot}02$ V.) and copper ($_{Cu}\epsilon_{q=0} = +0{\cdot}10$ V.). The final value of potential is equal to $+0{\cdot}25$ V., which is more positive than the null points of both iron and copper. Hence, at the beginning of contact exchange, the adsorption of cationic-type organic compounds is more probable while at the final stage that of anionic-type will take place. For suppressing contact exchange,

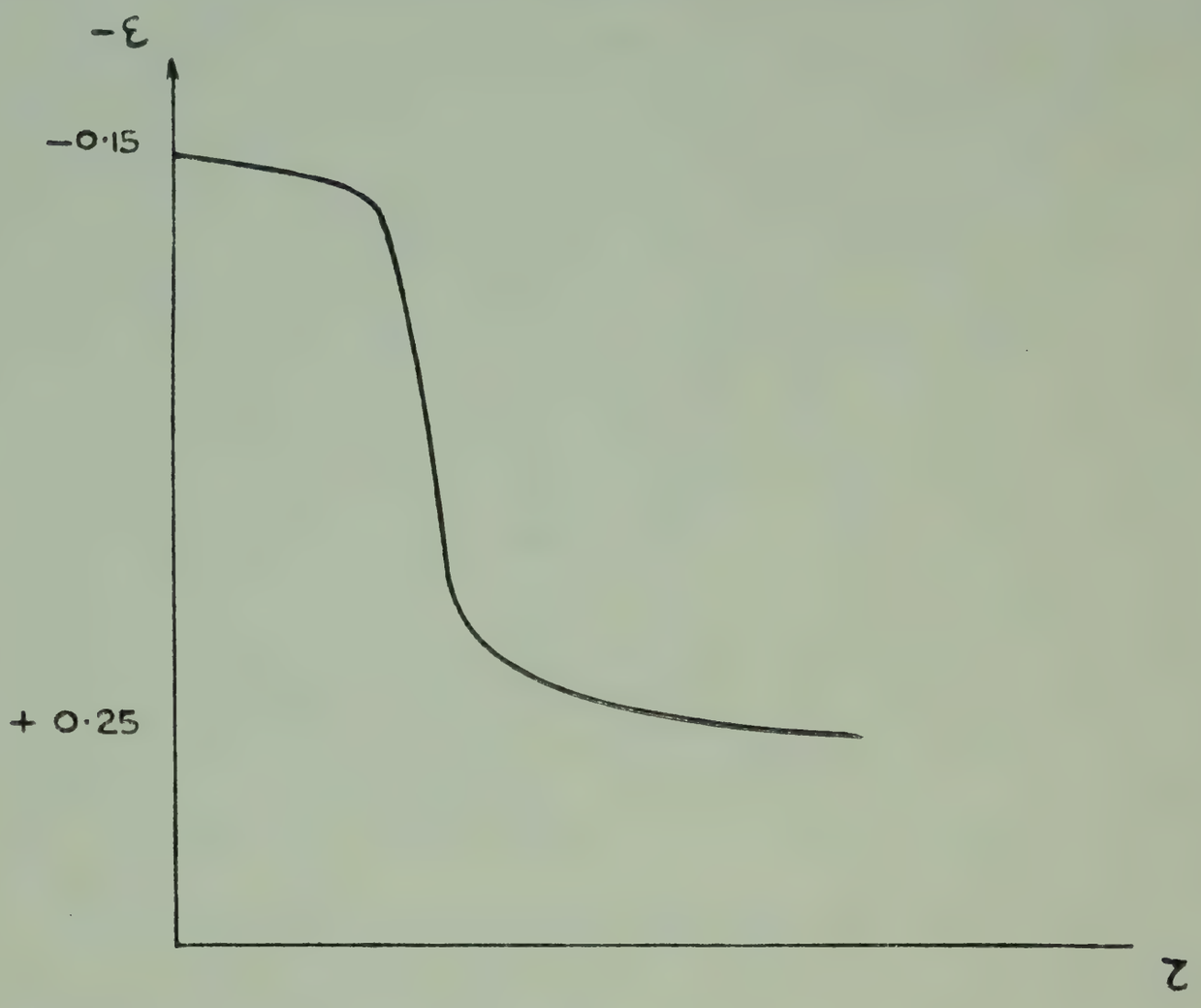

FIG. 33 — POTENTIAL-TIME CURVE OF THE PROCESS OF CONTACT EXCHANGE BETWEEN METALLIC IRON AND COPPER IONS IN SOLUTION

the use of a combination of both cationic and anionic surface active organic compounds is, therefore, suggested[155-157]. Fig. 34 shows the influence of tetrabutylammonium sulphate (cationic surface active organic compound) and thiourea (anionic surface active organic compound) added in a small amount into a copper sulphate bath on the anodic polarization of iron* and on the cathodic polarization of copper.

The rate of contact exchange at each stage of this process may be calculated on the basis of the following assumptions:

(i) The whole surface (S) is active and it is a sum of anodic area (S_a) and cathodic areas (S_k): $S = S_a + S_k$.

(ii) The surface of metal is equipotential.

Then, if the potential is known at a given moment (it can be obtained from the potential-time curve), the values of both

*The anodic polarization curves have been obtained in solutions of pure sulphuric acid with and without additions of the above organic compounds.

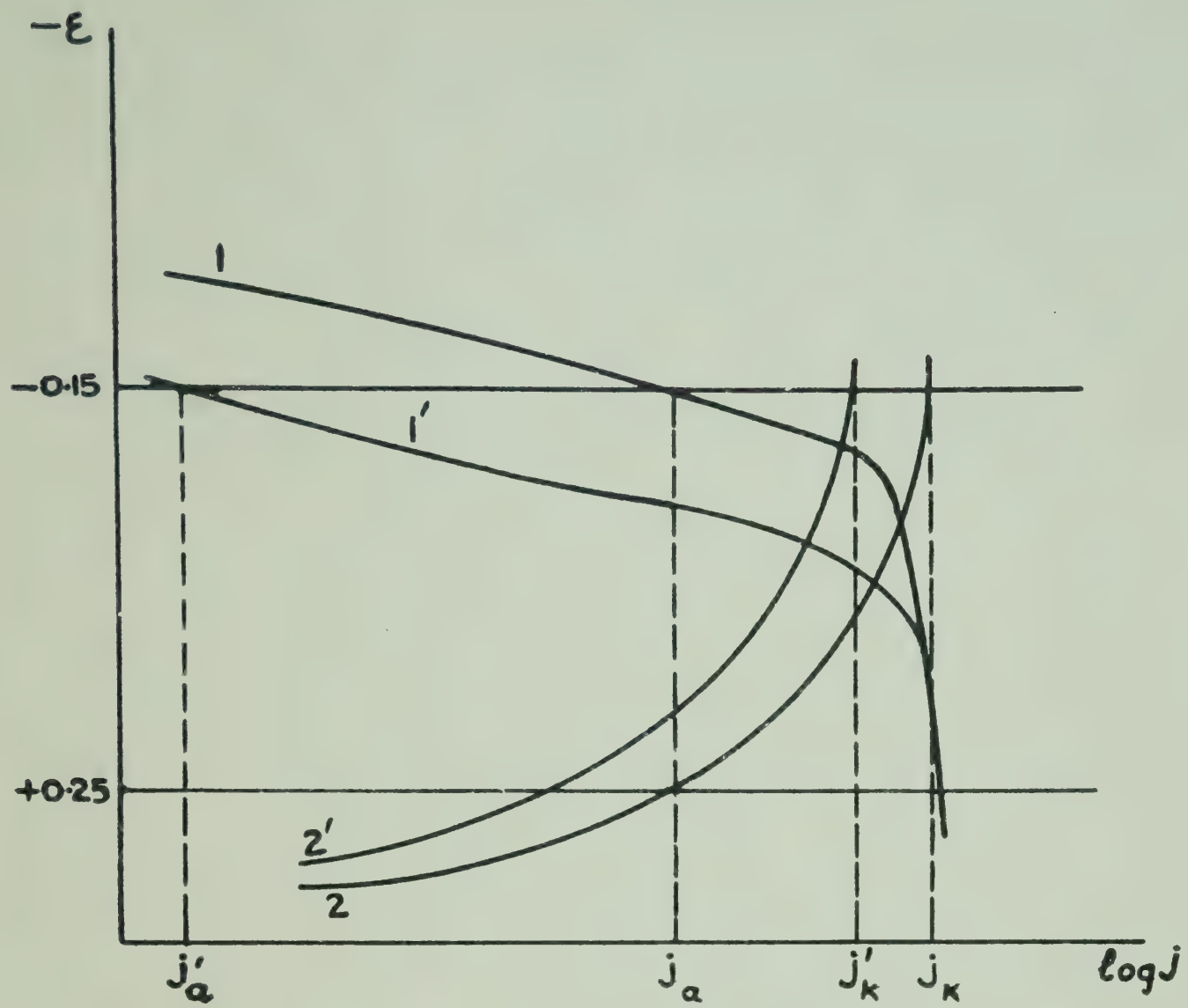

FIG. 34 — POLARIZATION CURVES OF IRON DISSOLUTION IN: (1) H_2SO_4 SOLUTION (100 g. H_2SO_4 PER LIT.) (1′) AND IN H_2SO_4 SOLUTION CONTAINING $CS(NH_2)_2$ + $[N(C_4H_9)_4]_2SO_4$ AND OF COPPER DEPOSITION FROM (2) $H_2SO_4 + CuSO_4$ AND FROM (2′) THE SAME SOLUTION WITH ADDITION OF $CS(NH_2)_2$ AND $[N(C_4H_9)_4]_2SO_4$

anodic (j_a) and cathodic (j_k) current densities may be found from the intersection of the polarization curves with the horizontal line which corresponds to the particular value of the potential (Fig. 34). It may be shown that the rate of exchange current j is equal to

$$j = j_a S_a = j_k S_k = \frac{j_a \times j_k}{j_a + j_k} \tag{68}$$

For the given example (additions of tetrabutylammonium sulphate and thiourea), the rate of contact exchange at the initial stage is equal to $1{\cdot}7 \times 10^{-2}$ and $\cdot 24 \times 10^{-4}$ A./cm.^{2} for the sulphate copper bath without and with the additions respectively. The

decrease of the exchange rate is more pronounced, if triphenylamine is used instead of tetrabutylammonium sulphate. In the presence of both these agents, copper plating may be carried out on iron and mild steel directly from the simple sulphate bath.

The same method may be applied in any case when a more noble metal is to be plated on the surface of a baser metal (e.g. silver on copper).

CONCLUDING REMARKS

1. As the author has been trying to show, throughout the present series of lectures, the main advantage of the φ-scale of potentials is that it provides a basis for a comparative study of various electrochemical rate processes on different electrodes. It enables particularly to utilize the data obtained on one electrode to interpret the results obtained on any other electrode if only the value of φ-potentials are equal or of the same order. The mercury electrode is ideal for carrying out many electrochemical experiments, such as, electrocapillary curves, differential double-layer capacity measurements, etc., both from the point of view of reproducibility and accuracy. The φ-scale of potentials gives a basis for application of these precise and easily obtainable data to a comprehensive treatment of kinetic phenomena on other electrodes. Thus, the value and importance of experiments with mercury electrodes is highly enhanced by the introduction of the φ-scale of potentials.

2. It would be entirely erroneous to consider the φ-scale as an antithesis of, or as a substitute for, the hydrogen scale of electrode potentials. The φ-scale should be always used in conjunction with, and in addition to, the common system of electrode potentials. In this case only it is possible to describe and give a clear and detailed picture of the electrochemical process. This may be illustrated by the following example: Consider an electrode at which a reaction of electroreduction of an organic compound is going on. The value of electrode potential as given on the hydrogen scale is equal to ϵ_1. Then, if the value of pH of the solution is known, the magnitude of hydrogen overpotential η_1 can be estimated. Thus, the deviation from the reversible state is given. At the same time the characteristic of reducing ability may be formulated as far as one of the participants in the electrode reaction — adsorbed hydrogen atoms, electrons or activated hydrogen ions — is concerned. But, neither the value of ϵ_1 nor that of η_1 (which, like the φ-potential, does not depend on the reference electrode chosen) gives any idea as to the conditions for the second participant — organic substance. If, however, the value of the

φ-potential is also given, then one can surmise the charge of the electrode with respect to the solution, as well as the surface concentration and the prevailing orientation of the organic compound. In the same manner, any other electrochemical rate process — electrodeposition and corrosion of metals, evolution of gases — might be more comprehensively understood if both the scales are used.

3. The φ-scale of potentials is based on the values of the null point of metals. Naturally, the degree of accuracy of φ-potential depends on how precisely the null points can be determined. Throughout these lectures it has been accepted that the null point of a metal is an important physical constant inherent to the metal, something like a melting point for instance. However, for some metals the apparent null point, as estimated by the differential capacity method, does not remain constant. Thus, for example, the potential corresponding to the minimum differential capacity of iron varies with the pH of solution. This can be ascribed to the formation of differently composed solid solutions of iron and hydrogen. It is natural to expect that the null point of a pure metal, like the melting point, differs from that of an alloy. In this case, for each process, the value of the null point should be taken with respect to the actual state of electrode. Fortunately, this variation is rather small and for many problems when φ-scale is applied, it is not very significant. It should be pointed out, however, that the nature of observed phenomenon is not yet clear, and that the measured capacities might, at least partly, be attributed to certain secondary effect connected with adsorbed and/or occluded hydrogen.

As stated above, the precision of the determination of null points is not very high. It may, therefore, be that some of the values of null points given here are not accurate enough and consequently, that some of the conclusions based on these values may also be incorrect. But it will not affect the general conception which these lectures are based upon. It will emphasize only that the elaboration of more precise methods for determination of null points and collection of reliable data on null points are of great importance to modern electrochemistry.

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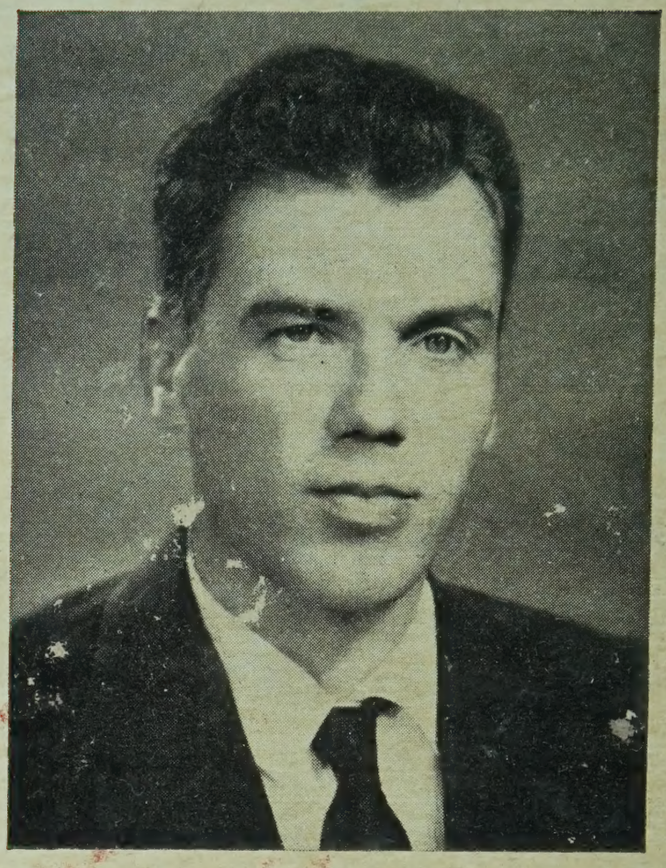

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